CHEMISTRY LIBRARY
Aug28 1957

JOURNAL
OF THE
INDIAN CHEMICAL SOCIETY

VOL. XXXIV APRIL, 1957 No. 4

CONTENTS

PAGE

46. Studies in sesquiterpenes. Part XV. Synthesis of 4-*iso*propyl-6-methoxy-tetralone-1.—By G. S. Krishna Rao and Sukh Dev 255
47. Organic reactions with polyphosphoric acid. Part V. Intramolecular acylation with lactones. *cyclo*Pentenones from δ-lactones.—By Sukh Dev and Charanjit Rai 266
48. Studies in the chemistry of tellurium. Part II. The electrodic behaviour of tellurium in buffer solutions of varying p_H.—By I. M. Issa, H. Khalifa and S. A. Awad 275
49. Polynuclear aromatic hydrocarbons. Part V. A new route to 3 : 4-benzfluorene derivatives.—By O. P. Vig, R. P. Gandhi and (Miss) R. K. Gulati ... 281
50. Synthesis of *p*-substituted α-bromo-α-formyl-acetophenones.—By H. G. Garg and M. M. Bokadia 286
51. Fries and Friedel-Crafts' reactions with methyl 2 : 4-dihydroxy-5-substituted benzoates and synthesis of 4-substituted 2-acylresorcinols.—By J. I. Setalvad and N. M. Shah 289
52. Experiments on the syntheses of furano compounds. Part XII. Further transformations of *iso*coumaranone.—By J. N. Chatterjea 299
53. Experiments on the syntheses of furano compounds. Part XIII. 1-Substituted dibenzofurans.—By J. N. Chatterjea 306
54. Studies on the metal complexes of hydroxamic acids. Part I. Spectrophotometric determination of manganese with nicotino- and *iso*nicotinohydroxamic acids.—By R. L. Dutta 311
55. Chemistry of beryllium. Part II. Compounds of beryllium chloride with amines.—By Sarju Prasad and Kashi Prasad Srivastava 317
56. Di-xanthones. Part I. Chromono-2 : 3-xanthone.—By Tara Singh and S. N. Bedi 321
57. Interaction of aromatic hydroxy ketones and their derivatives and thionyl chloride in presence of finely divided copper. Part XII. Preparation of 2 : 2′-dihydroxy-3 : 3′-diacetyl-4 : 4′-dimethoxydiphenyl thioether and derivatives.—By V. J. Dalvi and G. V. Jadhav 324
58. Monoterpenoids. Part II. Synthesis of 2-methyl-5-*iso*propylsuberone and 3 methyl-6-*iso*propylsuberone.—By T. M. Jacob and Sukh Dev 327
59. The electrical conductivity of aluminium oxide sols.—By A. K. M. Trivedi and K. M. Buch 337
60. Isolation of ursolic acid from *Vinca rosea* Linn.—By S. Roy and A. Chatterjee ... 340

Short Notes:

Aquo-ammino antimony chloride.—By H. K. Das and S. Pani 343
Effect of azotobacter on fixed nitrogen.—By M. A. Azim and Fazal Mohyuddin ... 344

PUBLISHED BY THE INDIAN CHEMICAL SOCIETY
92, UPPER CIRCULAR ROAD, CALCUTTA 9.

READY DELIVERY

"SIGCOL"

LABORATORY GLASSWARE

Made of

BOROSILICATE GLASS HAVING HIGH SILICA AND LOW ALKALI CONTENT WHICH ENSURES RESISTANCE TO THERMAL SHOCK AND CHEMICAL STABILITY

SARTORIUS

"SELECTA" BALANCES

Micro and Projection Types

CARL-ZEISS

REFRACTOMETERS

SPECTROPHOTOMETER

STEREO-MICROSCOPES

MUIRHEAD

POTENTIOMETER

"K-9"

TRIANGULAR BEAM

CIRCULAR ARRESTMENT

ANALYTICAL BALANCE

CAPACITY : 200 Gms.

SENSITIVITY : $\frac{1}{10}$ Mgm.

5 Divisions throw of pointer for addition of 1 Mgm.

CARL-ZEISS

HAND SPECTROSCOPES

POLARISING MICROSCOPES

METAL MICROSCOPES

POLARIMETERS

MICRO-PHOTO CAMERAS

LEYBOLD'S

VACUUM PUMPS

HERAEUS- OVENS

JULIUS PETER- BOMB CALORIMETER

HOPPLER- VISCOMETERS

Distributors :

ADAIR, DUTT & Co. (INDIA) PRIVATE Ltd.

CALCUTTA MADRAS BOMBAY NEW DELHI

THE INDIAN CHEMICAL SOCIETY

NOTICE

"Fellows of the Indian Chemical Society are requested to apply for the position of two research assistants in the Department of Chemistry, De Paul University, Chicago, U.S.A. One is at the Post-Doctorate level and carries a stipend of $ 3,600 to $ 4,000 per year depending on qualifications. The other is at the B.S. level at $ 1,800 per year. Both are tenable at the first instance for 12 months beginning September 1, 1957 or earlier, but may be extended to another year. The Junior Assistant will have full facilities (including remittance of tution fees) for the M. S. degree.

The post-doctorate candidate must possess a good record of academic career and research experience in *Organic Chemistry*. The B. S. level candidate must be a graduate with Honours in Chemistry.

The names of suitable candidates after preliminary choice will be forwarded to Professor Eugene Lieber, De Paul University, Illinois, U.S.A., under whom they will have to work, for final selection.

The applications stating academic career, research experience, research publications, if any, must reach the Hony. Secretary at the earliest convenience of the candidate.

Applications should be addressed to :

The Hony. Secretary,
INDIAN CHEMICAL SOCIETY,
92, Upper Circular Road,
CALCUTTA-9.

Information for Authors

1. All papers intended for publication in the Journal of the Indian Chemical Society should be addressed to the Hony. Secretary, Indian Chemical Society, 92, Upper Circular Road, Calcutta-9.

2. A paper will not normally be considered for publication in the Journal unless at least one of the authors or authors is (are) either a Fellow or an Associate member of the Society.

3. Communications which have appeared in any other journal shall not be published in this Journal unless this course is specially approved by the Council.

4. Normally an article or original paper should not exceed 15 foolscap pages. All papers should be submitted in typescript with double line and marginal spacings. Tables and foot-notes add considerably to the cost of printing ; authors are requested therefore not to use them unless necessary.

5. All papers should be carefully revised and should be absolutely in final form of printing. Positions for text-figures should be indicated. Authors are particularly requested to verify references. Authors are solely responsible for the factual accuracy of their papers.

6. Authors should note that the communications are meant for specialists in that field. Extensive review of literature should be avoided. Well known or previously published procedures followed in the experimental work should only be designated or referred to.

7. Periods of time (unless fractional) and quantities of material should be written in numerals. For economy the abbreviations, cm., c.c., ml., g., m.p., b.p., f.p., calc., exp., Fig., etc., should be used.

8. Authors are requested to enclose line drawings of the diagrams in their papers drawn in India ink on smooth white Bristol board. The drawings should be twice the size they will occupy in the Journal. Authors are particularly requested to reduce the number of diagrams and formulae to an absolute minimum. Organic structural formulae should be arranged to fill the space economically and arrows should be used horizontally or vertically, not diagonally, whenever possible.

9. The reference to literature should be given in brackets in the text and not as a foot-note or at the end and should conform to the normal usages of the *Journal* as regards order and punctuations, and to the abbreviations as given by Chemical Abstracts in its "List of Periodicals Abstracted". Thus, Name or names of authors, Name of Journal (abbreviated, with a single underline); year of publication; number of volume (double underline) and lastly page, e.g., Karrer and Schlieutz, *Helv. Chim. Acta*, 1934, **17**, 7.

The words and lines that will appear in italics in print should be underlined.

10. Authors are expected to be familiar with the normal rules of nomenclature but in case of doubt may refer to "Modern Chemical Nomenclature (Smith, *J. Chem. Soc.*, 1936, 1067).

11. New compounds should be indicated by underlining the name at its first mention (excluding Headings) in the experimental section and by giving analytical results in the form: "Found:———; ———. ——— requires ——— per cent". Analytical results for compounds which have been previously known should be given in the form: "Found:——; ——. Calc. for———; ———; ——."

12. Every paper should be accompanied by a short abstract giving briefly the objects of the investigation, the results obtained and their bearing on chemical knowledge in general. It should be such as to enable any chemist to obtain a clear idea of the investigation and normally should not exceed 250 words.

13. The address to which the proofs are to be sent should be written on every paper. One slip-proof or if possible a page-proof will be sent to authors, which should be returned whithin a week to the Hony. Secretary, failing which it will be directly printed.

14. Authors will get 50 copies of reprints free of charge and extra 25 copies on payment of Re. 1/- per page. Extra copies of reprints over 75 copies will be charged at Rs. 5/- per page. Cost of paper and binding extra. If extra copies are required, the author should intimate the Hony. Secretary, at the time of returning the corrected proofs. It would be desirable to inform him when the manuscript is sent.

15. **Notes will be given priority in publication.**

Change of address should be immediately intimated to the office.

No claims will be allowed for copies of Journal lost in the mail or otherwise, unless such claims are received within 90 days of the date of issue.

	Inland rates.	Foreign rates.	
		Sterling area	Dollar area
Cost of Single Issue Rs.	3		
Annual Subscription ,,	20 (for Fellows)	20	25
,,	24 (for Subscribers)	28	32
,,	28 (Composite)	34	40

Inland Rates of Advertisement

In Ordinary Pages:
(Single insertion)

Full Page	... ...	Rs. 40/-
Half Page	... ...	,, 25/-
Quarter Page	... ...	,, 15/-

In Cover Pages :		In special positions :	
Cover (Back) Full	... Rs. 100/-	Page facing first reading matter	... Rs. 70/-
,, ,, Half	... ,, 60/-	Page facing last page of reading matter	... ,, 60/-
Second and Third Pages :			
Full Page	... Rs. 70/-	Page facing inside front cover	... ,, 50/-
Half Page	... ,, 40/-	Page facing inside back cover	... ,, 50/
Quarter Page	... ,, 25/-		

Closing date for advertising materials: 7th of the previous month.

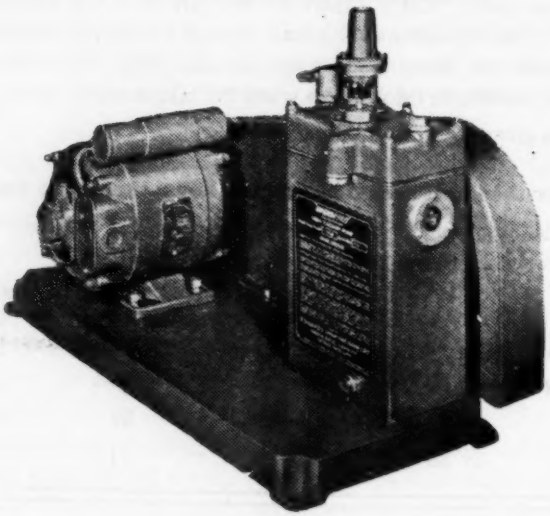
10% *Rebate allowed in cases of six consecutive full and half page insertions.*

All communications are to be addressed to :

The Hony. Secretary,
INDIAN CHEMICAL SOCIETY
92, Upper Circular Road, Calcutta-9.

EDWARDS

"SPEEDIVAC" ROTARY GAS BALLAST VACUUM PUMPS



Ideal for:-

Vacuum Filtration : Baking Degassing : Dehydration : Concentration : Distillation : Melting : Processing

The Gas Ballast system provides suitable safeguard for mechanical pumps against contamination of the pump oil by vapour present in the vacuum outfit which causes lengthening of pumping down time, deterioration of the ultimate vacuum and necessitates frequent renewal of oil. Precautions in the past against these evil effects of the contamination involved the use of chemical or refrigerated traps, oil purifiers, etc., which added considerably to the cost and complication of the process. With gas ballast mechanical pumps can handle a wide variety of vapours with practically no risk of contamination of the oil. If for any reason contamination does occur, the gas ballasted pump can purify its own oil charge, often as good as new.

DISTRIBUTORS:

THE SCIENTIFIC INSTRUMENT Co. Ltd.

ALLAHABAD, BOMBAY, CALCUTTA, MADRAS, NEW DELHI.

[Jour. Indian Chem. Soc., Vol. 34, No 4, 1957]

STUDIES IN SESQUITERPENES. PART XV. SYNTHESIS OF 4-*iso*PROPYL-6-METHOXYTETRALONE-1

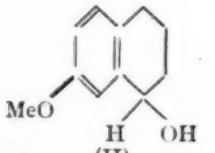
By G. S. Krishna Rao and Sukh Dev

The preparation of 4-*iso*propyl-6-methoxytetralone-1, a potential intermediate in the synthesis of cadinene, is reported.

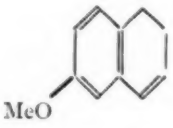
For the synthesis of cadinene, 4-*iso*propyl-6-methoxytetralone-1 (I) appears to be an attractive intermediate ; its preparation has been described in the present communication.

The starting material for the synthesis of (I) was 7-methoxytetralone-1 (XIII), which was, in turn, obtained by the ring-closure of γ-(*p*-methoxyphenyl)-butyric acid (XII). Useful modifications (vide Experimental) were effected in its preparation, resulting in much economy in time. The intramolecular acylation of the acid (XII) was most conveniently carried out by the application of polyphosphoric acid (Sukh Dev, this *Journal*, 1955, **32**, 257).

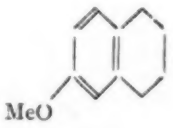
The next step was the preparation of the tetralin (XIX) from the tetralone (XIII) ; the straightforward synthesis involving its reaction with *iso*propylmagnesium halide could not be accomplished as the reaction always gave a mixture consisting of the unchanged tetralone, its reduction product the tetralol (II), and high boiling condensation products. The absence of the Grignard-addition product was established by a study of the dehydration of the crude reaction product ; the elimination reaction was not quite facile and the product consisted almost entirely of the dialin (III) ; this hydrocarbon was identified by its hydrogenation to the tetralin (IV) which on chromic acid oxidation (Burnop *et al.*, *J. Chem. Soc.*, 1940, 730 ; Stork, *J. Amer. Chem. Soc.*, 1947, **69**, 576; Thomas and Nathan, *ibid.*, 1948, **70**, 331) furnished the crystalline ketone (V). This condensation could not be effected by the use of either *iso*propylmagnesium iodide (Shine, *J. Chem. Soc.*, 1951, 8) or *iso*propyllithium (Young and Roberts, *J. Amer. Chem. Soc.*, 1944, **66**, 1444).



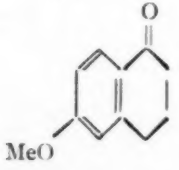
(II)



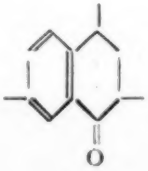
(III)



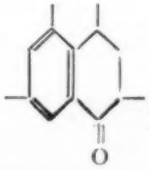
(IV)



(V)



(VI)

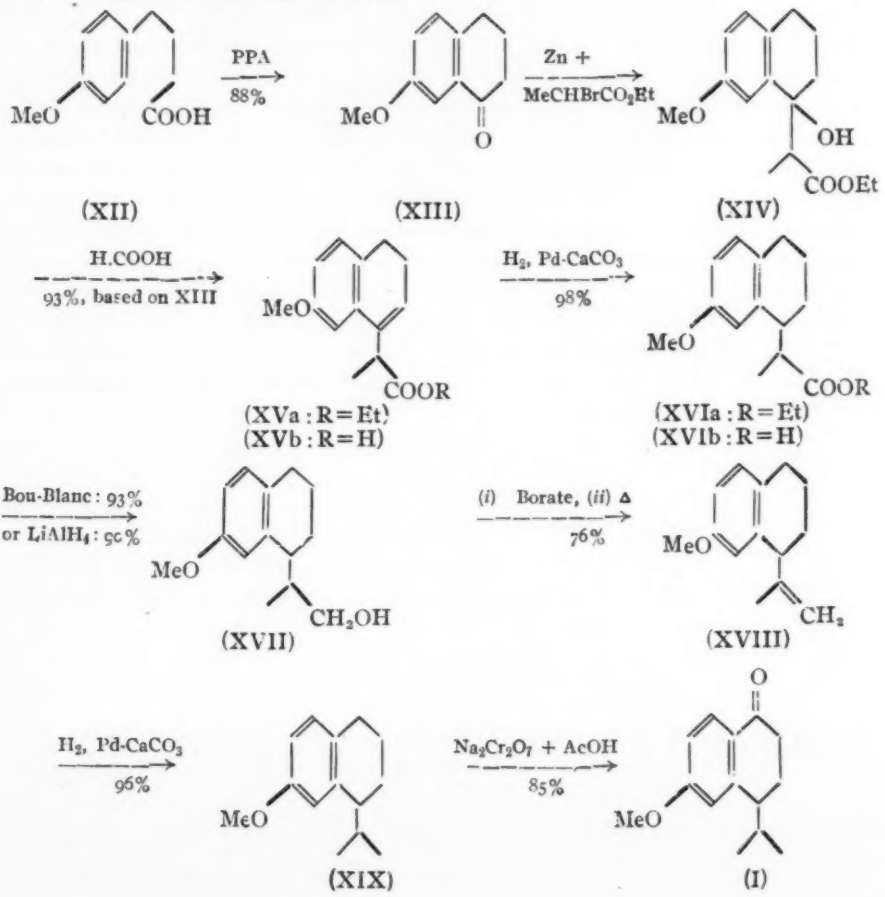


(VII)

The reaction of *iso*propylmagnesium bromide with 2:4:7-trimethyltetralone-1 (VI) (Sukh Dev, this *Journal*, 1948, **25**, 69) or 2:4:5:7-tetramethyltetralone-1 (VII) (Gupta and Muthana, *J. Indian Inst. Sci.*, 1953, **35**, 310) has been reported to proceed in a normal fashion. In the present case, it is rather difficult to see, why this anomalous reaction takes precedence. A study of the space model (Catalin Molecular Models) of 7-methoxytetralone-1 (XIII) showed the absence of any steric hindrance at the carbonyl function. The induction effect ($-I_s$) of the methoxy group is not expected to be appreciable at the site of the keto group.

A number of similar cases have been recorded in the literature. Thus, 5:8-dimethyltetralone-1 (Cocker *et al.*, *J. Chem. Soc.*, 1953, 2355), 4:7-dimethylindanone-1 (Herz, *J. Amer. Chem. Soc.*, 1953, **75**, 73), 6-methylindanone-1 (Wagner-Jauregg, Arnold and Huter, *Ber.*, 1942, **75B**, 1293) and 4:6-dimethylindanone-1 (Wagner-Jauregg and Hippchen, *Ber.*, 1943, **76B**, 694) have all been shown to undergo the abnormal reaction with *iso*propylmagnesium halide.

Since this route to 1-*iso*propyl-7-methoxytetralin (XIX) failed, an alternative synthesis, as outlined below, was developed.

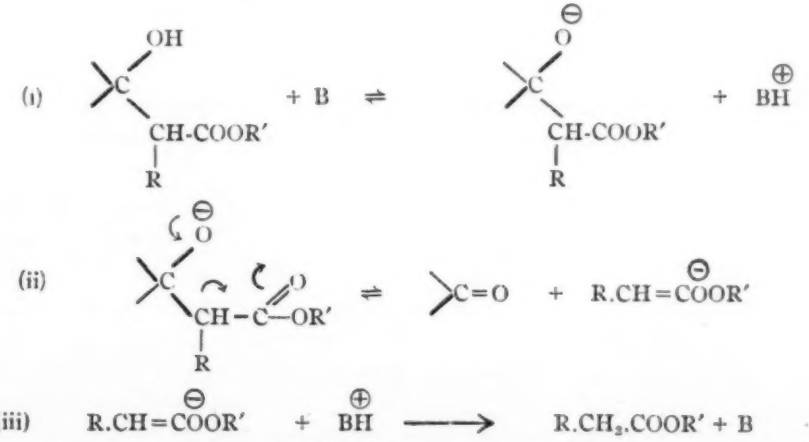


The Reformatsky reaction of 7-methoxytetralone-1 with ethyl α-bromopropionate yielded the hydroxy-ester (XIV) in an excellent yield. This condensation was studied previously by Paranjape, Phalnikar and Nargund [*J. Univ. Bombay*, 1943-4, **12** (N. S.), Part 3, p. 60], but no details were published. The crude hydroxy-ester on attempted distillation underwent retrogression * and hence was as such dehydrated with 90% formic acid, when the unsaturated ester was obtained. The product displayed three maxima (vide Experimental) in the U. V. regions characteristic of the styrene-system with a *m*-hydroxyl substituent (Dorfman, *Chem. Rev.*, 1953, **53**, 96; Sandoval *et al.*, *J. Amer. Chem. Soc.*, 1955, **77**, 148). Based on this evidence, the product has been assigned the structure (XVa). It is of interest to note that during the course of a dehydration experiment, an inadvertent use of weak formic acid (about 20%) led to the cleavage of the Reformatsky product (XIV) with the regeneration of the starting ketone (XIII). Similar cases have been recorded in the literature (Shriner in "Organic Reactions", John Wiley & Sons Inc., New York, 1942, Vol. I, p. 14)*.

Catalytic hydrogenation smoothly yielded the reduced ester (XVIa). The carbethoxy group in (XVIa) was converted into the corresponding primary alcohol by lithium aluminium hydride or by Hausley's modification (*Ind. Eng. Chem.*, 1947, **39**, 55) of the Bouveault-Blanc reduction; both procedures afforded excellent yields of the desired product (XVII). The alcohol was dehydrated *via* its borate ester (Brandenberg and Galat, *J. Amer. Chem. Soc.*, 1950, **72**, 3275; O'Connor and Nace, *ibid.*, 1953, **75**, 2118) to provide the olefin (XVIII) in a good yield. The product displayed two weak maxima at

---

* Heat (Wallach, *Annalen*, 1909, **365**, 255), alkalies (Bachmann *et al.*, *J. Amer. Chem. Soc.*, 1940, **62**, 824) and acids (Reformatsky, *J. Russ. Phys. Chem. Soc.*, 1898, **30**, 280; *J. prakt. Chem.*, 1896, **54**, 477; Sörm and Mleziva, *Coll. Czech. Chem. Comm.*, 1949, **14**, 98) have been known to be capable of effecting the cleavage of the β-hydroxy-acids or their esters derived from a Reformatsky condensation. It appears reasonable to assume that with a base the cleavage reaction possibly proceeds as depicted below:



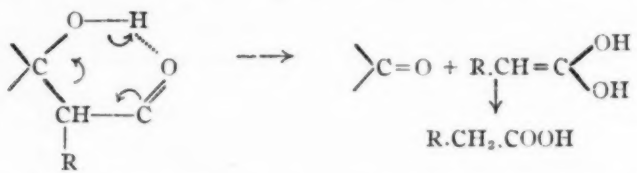
(Continued to next page Footnote.)

255mμ and 280 mμ. Whereas the latter band is to be ascribed to the anisol system (Dorfman, *loc. cit.*), the absorption at 255mμ is rather unexpected and it is likely that the material may be contaminated with the corresponding *iso*propylidene isomer, which is expected to absorb (cf. Juday, *J. Amer. Chem. Soc.*, 1953, **75**, 3008) strongly at about 10 mμ towards the shorter wave-lengths as compared to the chromophore in (XVa). The olefin on hydrogenation over Pd-$CaCO_3$ catalyst furnished the desired 1-*iso*propyl-7-methoxytetralin (XIX). This synthesis enabled us to prepare (XIX) in an overall yield of 62% based on the tetralone (XIII).

In view of the known chromic acid oxidation (Burnop *et al.*, *loc. cit.*; Stork, *loc. cit.*; Thomas and Nathan, *loc. cit.*) of 6-methoxytetralin (IV) to the tetralone (V), and a number of other similar recorded instances (McNiven, *J. Amer. Chem. Soc.*, 1954, **76**, 1725; Buchi and Pappas, *ibid.*, 1954, **76**, 2963; Ritchie *et al.*, *ibid.*, 1954 **76**, 723) of oxidation, it was anticipated that 4-*iso*propyl-6-methoxytetralone-1 (I) could be easily obtained from the tetralin (XIX) by such an oxidation. This was readily realised and the ketone could be prepared in a yield of 70-75%. The yield of the tetralone could be raised to 85% by the use of sodium dichromate-acetic acid mixture (Corey and Ursprung, *J. Amer. Chem. Soc.*, 1956, **78**, 183; Fieser, *ibid.*, 1953, **75**, 4386). Oxidation of the tetralin (XIX) by hydrogen peroxide in presence of vanadium pentoxide (Treibs *et al.*, *Ber.*, 1953, **86**, 616) afforded the ketone in 19% yield only. The structure (I) for this ketone is supported by the light absorption data (Fig. 1). As expected, the position of the maximum is identical with that of 6-methoxytetralone-1 (V).

---

*(Contd.) For thermal fission, the following transition state appears attractive :



In the case of a cleavage in acid media, the reaction can be rationalised as under :

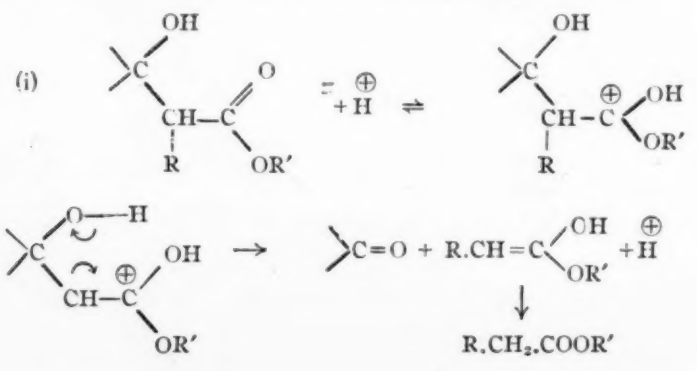
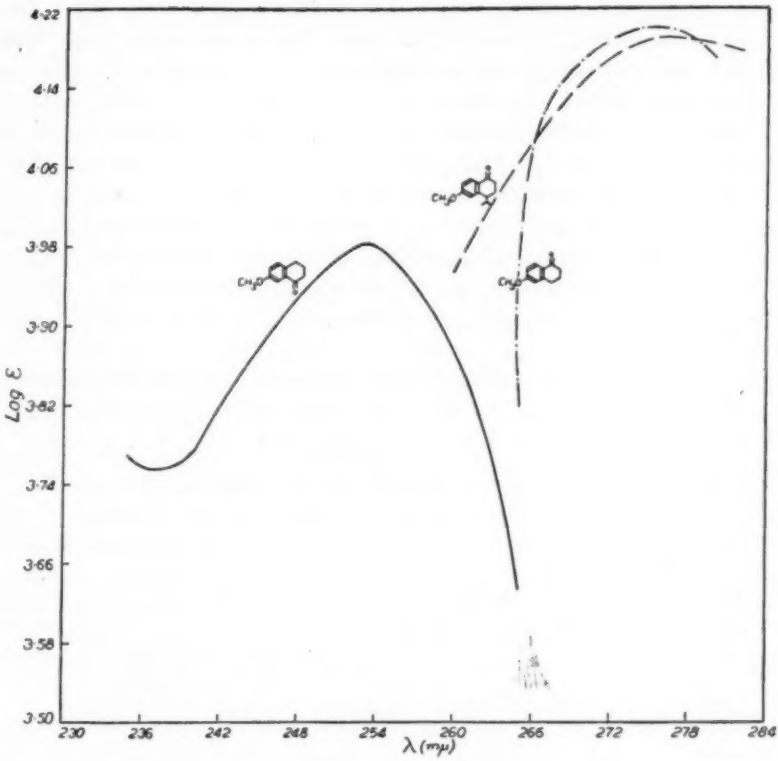


FIG. 1



Work on the conversion of 4-*iso*propyl-6-methoxytetralone-1 into cadinene is being pursued.

EXPERIMENTAL

All melting and boiling points are uncorrected. Petroleum ether refers to the fraction with the boiling range 40°-60°. The solvent extracts were dried over anhydrous Na_2SO_4. The spectra were taken on a Beckman DU spectrophotometer.

β-(p-*Anisoyl*)-*propionic Acid*.—The following procedure was found to be more convenient (cf. Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1936, **58**, 2315 ; Dauben and Adams, *ibid.*, 1948, **70**, 1759).

Anisol (108 g., 1 *M*), succinic anhydride (110 g., 1.1 *M*) and dry nitrobenzene (500 c.c.) were placed in a 3-litre 3-necked flask, carrying a slip-sealed stirrer and a calcium chloride guard-tube. The mixture was chilled in ice-salt and with stirring was introduced anhydrous aluminium chloride (293 g., 2.2 *M*) in four lots during 1½ hours. The reaction mixture was stirred at the ice-bath temperature for 3 hours and then replenished the ice-bath and left aside overnight (12 hours). Next day it was

again stirred at room temperature (25°) for 6 hours and the rose-coloured reaction mixture was poured on ice (1.5 kg.) and HCl (400 c.c.). Due to sparing solubility in nitrobenzene, most of the acid separated out and was filtered off and washed with benzene-ether mixture (1.1 ; 100 c.c. × 4). From the filtrate, the solvent layer was separated and the aqueous portion extracted with ether (100 c.c. × 3). The combined solvent extracts were washed with water (200 c.c. × 1) and the keto-acid was extracted out with aqueous sodium hydroxide (10% ; 50 c.c. × 3). Acidification of the alkaline solution gave some more (15-20 g.) acid. The combined crude keto-acid was thoroughly washed with water and dissolved in ammonium hydroxide (15%), the solution was boiled for 2 hours (with occasional addition of water to prevent undue concentration) to drive off traces of nitrobenzene and after clarification with active carbon, was acidified to furnish the desired product as a white crystalline solid, m.p. 144-47° (Fieser and Hershberg, *loc. cit.*, m.p. 147-48°), yield 190 g. (91%). The material was used as such for the next step.

γ-(p-*Anisyl*)-*butyric Acid* (XII).—The Clemmensen reduction of the above keto-acid was effected in the following much less time-consuming manner (cf. Martin, "Organic Reactions", John Wiley & Sons, Inc., New York, 1942, Vol. I, p. 167).

Zinc wool (175 g.) was amalgamated with mercuric chloride (17.5 g.), HCl (20 c.c.) and water (175 c.c.) by shaking for 10 minutes and decanting off the aqueous solution. To this the above keto-acid (140 g.) and HCl (conc., 1200 c.c.) were added. While the mixture was gently refluxed for 5 hours, HCl (conc., 280 c.c.) was introduced portion-wise each hour. The hot reaction mixture was filtered off through a plug of glasswool ; the unchanged zinc was washed with boiling water (100 c.c. × 4). From the filtrates the reduced acid that had crystallised out was collected. The zinc wool was washed with warm sodium bicarbonate solution (10% ; 100 c.c. × 2) and acidification of the alkaline washings yielded a further quantity of the desired acid. The combined γ-(*p*-anisyl)-butyric acid was powdered and well washed with water and dried. This was distilled to yield the pure acid, b.p. 161-63°/1 mm, m.p. 61-62°, in 120 g. (92%) (Martin, *J. Amer. Chem. Soc.*, 1936, **58**, 1438, reports m.p. 61-62°).

7-*Methoxytetraione*-1 (XIII).*—Polyphosphoric acid (PPA), prepared from P_2O_5 (270 g.) and syrupy phosphoric acid (*d* 1.75, 116 c.c.) in an 1-litre 3-necked flask fitted with a Hershberg stirrer, was maintained at a temperature of 80° for 1 hour and the molten γ-(*p*-anisyl)-butyric acid (90 g., 0.49 *M*) was added in one lot. This was thoroughly stirred at this temperature for 5 minutes and the homogeneous reaction mixture was left aside at 80° for another 25 minutes *without* stirring. The reddish brown product, while still hot, was at once poured on crushed ice containing some ether (100 c.c.). For the sake of convenience, the material was left aside overnight to decompose the complex. The product was taken up in ether (80 c.c. × 4), washed with water (25 c.c. × 2), aqueous NaOH (5% ; 25 c.c. × 2) and brine (20 c.c. × 3). The neutral solution was dried, the solvent distilled off (column) and the residue purified by distillation, b.p. 130-32°/0.5 mm, m.p. 66-67°, yield 72 g. (88%) (lit., *loc. cit.*, m.p. 66-67°). λ_{max}^{EtOH} 253 mμ (ε, 9580).

*For references see " Encyclopaedia of Organic Chemistry", Elesevier Publishing House, Amsterdam, 1940, 12 B, p. 2666.

The 2 : 4-*dinitrophenylhydrazone* (H_2SO_4 method) was obtained as glistening deep orange-red rods from pyridine, m.p. 278° (decomp.). (Found : N, 15.64. $C_{17}H_{16}O_5N_4$ requires N, 15.73%).

Action of iso*Propylmagnesium Bromide on* (XIII).—In a typical experiment, a solution of 7-methoxytetralone-1 (8.8 g., 0.05 *M*) in ether (50 c.c.) was gradually introduced with continuous swirling to a well-cooled (ice-bath) solution of *iso*propylmagnesium bromide (from Mg 1.55 g., 0.064 g. atom, *iso*propyl bromide 8 g., 0.065 *M* and ether 80 c.c.). As each drop of the ketone solution came in contact with the Grignard solution, a red colour developed, which vanished immediately on swirling. From the clear pale green solution no solid complex separated (even after standing). The reaction mixture was left overnight (12 hours) and then refluxed for 1½ hours. The cooled reaction mixture was decomposed by pouring on ice and H_2SO_4 (10 c.c.). The ether layer was separated and the aqueous portion extracted with ether (20 c.c. × 3). The extracts were washed with water and dried. Removal of the solvent furnished a viscous liquid residue (9.0 g.).

This material (0.28 g.) on treatment with 2 : 4-dinitrophenylhydrazine reagent yielded the 2 : 4-dinitrophenylhydrazone of 7-methoxytetralone (0.18 g.), m.p. 275-77°, undepressed by an authentic sample. This showed that the material contained about 34% of 7-methoxytetralone.

Another portion (8.0 g.) was added slowly (1 hour) to freshly fushed sodium hydrogen sulphate (0.5 g.) contained in a 10 c.c. modified Claisen flask, maintained at 160-70° and arranged for vacuum distillation. The distillate (3.8 g.) came over at 97-113°/1 mm and a polymeric residue was left. The volatile material was fractionated to furnish two fractions : (*i*) b.p. 94-97°/2 mm, 1.0 g. and (*ii*) b.p. 106-120°/2 mm, η_D^{32} 1.5585, 2.7 g. The first fraction was redistilled over sodium to afford a mobile liquid, b.p. 93-95°/1 mm, η_D^{30} 1.5745, yield 0.6 g. (Found : C, 82.19 ; H, 7.96. $C_{11}H_{12}O$ requires C, 82.5 ; H, 7.5%). That this material was essentially 7 *methoxy*-3 : 4-*dihydronaphthalene* (III) was established by catalytic hydrogenation over palladium on calcium carbonate to 7-*methoxytetralin* (IV) (b.p. 109-11°/4 mm, η_D^{30} 1.5405, yield 70%), which was in turn oxidised by chromic acid in acetic acid to 6-*methoxytetralone* (V), m.p. 78-79° (benzene-petroleum ether) ; mixed m.p. with an authentic sample was not depressed. The second fraction, which failed to solidify, but gave a positive test with 2 : 4-dinitrophenylhydrazine and reacted with sodium, was presumably a mixture of the tetralone (XIII) and the tetralol (II).

Ethyl 1-*Hydroxy*-7-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-1-α-*propionate* (XIV). —The procedure was patterned after that of Bachmann and Wendler (*J. Amer. Chem. Soc.*, 1946, **68**, 2582).

Freshly cut, clean zinc-wool (25.5 g., 0.39 g. atom) was covered with thiophene-free benzene (200 c.c.) and the 7-methoxytetralone (56.0 g., 0.35 *M*) was added. The mixture was refluxed and some solvent (about 50 c.c.) was tapped off to remove the last traces of the moisture from the system. This was cooled, and dry ether (100 c.c.) together with 1/5th of ethyl α-bromopropionate (75.6 g., 0.39 *M* ; 54 c.c.) was intro-

duced. The reaction was initiated by warming and adding a crystal of iodine. After the reaction had started, the balance of the bromo-ester was let in during 1½ hours. The reaction mixture was gently refluxed till all the zine had disappeared (6 to 15 hours). After heating for another 2 hours, the product was cooled (0°) and glacial acetic acid (35 c.c.) and water (175 c.c.) were added cautiously. The solvent layer was separated and washed with dilute acetic acid (10%, 90 c.c.), followed by washing with brine containing ammonium hydroxide. Removal of the solvent yielded the crude hydroxy-ester (91.8 g.) as a viscous liquid. An attempt to fractionate the crude ester under reduced pressure at 2 mm ended up in an almost quantitative recovery of the starting 7-methoxytetralone-1 (*vide supra*). It was hence directly dehydrated as follows.

Ethyl 7-Methoxy-3 : 4-dihydronaphthalene-1-α-propionate (XVa).—A mixture of the above crude hydroxy-ester (91.8 g.) and formic acid (90%, 184 c.c.) was heated by immersing in a boiling water-bath for 1 hour. The product was cooled, diluted with water (500 c.c.) and extracted with petroleum ether (80 c.c. × 3). The combined extracts were washed with water (25 c.c. × 2), aqueous sodium bicarbonate (10% ; 30 c.c. × 3), finally with brine (20 c.c. × 2) and dried. This was stripped off the solvent and the residue fractionated (Vigreux column, 10″) to afford the unsaturated ester (XVa) as a somewhat viscous liquid with a faint yellow tinge, b.p. 164-66°/2 mm, η_D^{28} 1.5435, yield 75 g. (93%) (Paranjape *et al., loc. cit.*, report b.p. 175°/25 mm).

An analytical sample (central cut) had b.p. 152°/1 mm, $\eta_D^{28.5}$ 1.5435, $d_4^{28.5}$ 1.090, M_D 75.28 (calc. 73.11, $E\Sigma_D$ 0.84) ; λ_{max}^{EtOH} 220 mμ (ε, 21380), 261mμ (ε, 6030) and 305 mμ (ε, 2960). (Found : C, 73.89 ; H, 7.94. $C_{16}H_{20}O_3$ requires C, 73.85 ; H, 7.69%).

Saponification of the ester (2 g.) by refluxing with NaOH (1.6 g.) in water (5 c.c.) and ethanol (8 c.c.) for 3 hours afforded the corresponding acid (XVb), m.p. 110-12°, in a quantitative yield. Two crystallisations from dilute acetic acid furnished long, white rods, m.p. 117° (Paranjape *et al., loc. cit.*, described as a liquid, b.p. 215°/25 mm). (Found : C, 72.18 ; H, 6.84. $C_{14}H_{16}O_3$ requires C, 72.41 ; H, 6.90%).

Ethyl 7-Methoxytetralin-1-α-propionate (XVIa).—The above unsaturated ester (XVa : 42 g.) in ethanol (50 c.c.) was shaken with pre-reduced Pd-$CaCO_3$ (Busch *et al., Ber.*, 1916, **49**, 1063 ; 1929, **62**, 1458) (5 g.) in an atmosphere of hydrogen at laboratory temperature and pressure. The reduction came to a close after 2 hours when 101% of the theoretical quantity of hydrogen had been absorbed. The catalyst was removed by filtration and washed with ether (50 c.c.). The solvent was removed from the filtrate through a column under slight suction. Fractionation of the residue furnished the required product (XVIa) as a colorless, viscous liquid, b.p. 160 62°/2 mm, η_D^{27} 1.5245, yield 41.4 g. (98%).

An analytical sample had η_D^{30} 1.5210, d_4^{30} 1.067, M_D 74.74 (calc. 73.58, EM_D 1.16, $E\Sigma_D$ 0.44). (Found : C, 73.26 ; H, 8.45. $C_{16}H_{22}O_3$ requires C, 73.28 ; H, 8.40%).

A sample (0.5 g.) of this ester was hydrolysed as above to furnish the *saturated acid* (XVIb), m.p. 70-76°, yield 0.2 g. After three crystallisations from benzene-petroleum ether, it was obtained as stout, white prisms, m.p. 85°. (Found : C, 72.25 ; H, 7.94. $C_{14}H_{18}O_3$ requires C, 71.79 ; H. 7.69%).

An attempt to prepare the saturated acid directly from the unsaturated ester (XVa) by the Raney-nickel alloy-alkali method (Sukh Dev, this *Journal*, 1955, **32**, 513) resulted only in the isolation of the unsaturated acid (XVb).

β-1-(7-Methoxy-1 : 2 : 3 : 4-tetrahydronaphthyl)-n-propanol (XVII) : (*i*) *By Lithium Aluminium Hydride Reduction.*—The above saturated ester (XVIa : 5.24 g., 0.02*M*) in ether (25 c.c.) was reduced with a slurry of $LiAlH_4$ (0.95 g., 0.025 *M*) in ether (25 c.c.) in the usual manner, and worked up with 10% H_2SO_4 (70 c.c.) at below 0°. The alcohol (XVII) was isolated as a colorless, thick liquid, b.p. 150-52°/0.8 mm, η_D^{26} 1.5510, d_4^{26} 1.081, M_D 64.89 (calc. 64.21), yield 3.94 g. (90%). (Found : C, 76.25 ; H, 9.0. $C_{14}H_{20}O_2$ requires C, 76.36 ; H, 9.09%).

(*ii*) *By Bouveault-Blanc Reduction.*—Bright sodium (37 g., 1.62 g. atom ; 50% excess) was placed in a dry 3-necked flask, fitted with a Hershberg slipseal stirrer, a condenser, a dropping funnel and connected to a system for maintaining nitrogen atmosphere. The sodium was immediately covered with anhydrous toluene (75 c.c.) and heated in an oil-bath at 120° and stirred to disperse the sodium. A mixture of the saturated ester (XVIa : 72 g., 0.27 *M*), anhydrous *tert.*-butanol (72 g., 1.0 *M*) and toluene (100 c.c.) was added during 1 hour with stirring under nitrogen atmosphere. The bath temperature was maintained at 120° ± 5° throughout the addition. The stirring and heating were continued for a further period of 30 minutes. The product was cooled, finally in an ice-bath and cautiously treated with small lots of ice-water with swirling. After 250 c.c. of water had thus been introduced, the toluene layer was separated and washed with water (50 c.c. × 4). The alkaline washings and the previous aqueous portion were mixed and extracted with ether (75 c.c. × 3). The combined solvent extracts were washed with dilute acetic acid (5% ; 100 c.c. × 1) and finally with brine (75 c.c. × 2). After drying, the solvents were fractionated off and the residue distilled (column) : b. p. 152°/0.8 mm, $\eta_D^{26.5}$ 1.5510, yield 55 g. (93%). In this preparation the inert atmosphere is necessary to avoid the discoloration of the reaction mixture towards the end, with the consequent loss in the yield.

2-(7-Methoxy 1 : 2 : 3 : 4-tetrahydronaphthyl-1)-propene (XVIII).—A mixture of the above alcohol (55 g., 0.25 *M*), boric acid (15.5 g., 0.25 *M*) and toluene (150 c.c.) was gently refluxed, in an apparatus suitable for the continuous removal of water, till no more water (9 c.c.) had separated (3 hours). The heating was continued for another 15 minutes during which period some toluene (20 c.c.) was tapped off. The apparatus was disconnected and the toluene was distilled off under reduced pressure (water pump). The residue was pyrolysed at an inside temperature of 330° at 1.5 mm pressure ; under these conditions the distillation of the pyrolysate was quite smooth. The distillate (b.p. 116°-140°/1.5 mm) together with the condenser-washings was taken up in petroleum ether and dried over activated silica gel (10 g.). The solvent was removed and the residue fractionated over sodium (5 g.). The desired product was obtained as a colorless, fairly mobile liquid, b.p. 130-34°/4mm, η_D^{24} 1.5475, yield 38.6 g. (76.4%).

An analytical sample had b.p. 130°/4mm, η_D^{26} 1.5455, d_4^{26} 1.006, M_D 63.48 (calc. 62.23); λ_{max}^{EtOH} 255 mμ (ε, 2250) and 280 mμ (ε, 2730). (Found : C, 83.3 ; H, 8.71. $C_{14}H_{18}O$ requires C, 83.3 ; H, 8.91%).

1-iso*Propyl-7-methoxytetralin* (XIX).—The above unsaturated material (XVIII: 38.6 g.) in ethanol (40 c.c.) was shaken with pre-reduced Pd-$CaCO_3$ (Busch, *loc. cit.*) (3.8 g.) in an atmosphere of hydrogen at ordinary temperature and pressure, when the theoretical amount of hydrogen was absorbed in 8 to 9 hours. The rate of hydrogenation, which was very fast in the first hour, slowed down considerably towards the end. On working up as described under (XVIa) and fractionation over sodium, the required tetralin was obtained as a colorless, mobile liquid, b.p. 118-20°/1.5 mm, $\eta_D^{29.5}$ 1.5365, yield 37.3 g. (96%).

A refractionated specimen (central cut) had b.p. 103-104°/0.5 mm, η_D^{26} 1.5340, d_4^{26} 1.007, M_D 63.25 (calc. 62.69, $E\Sigma_D$ 0.28). (Found: C, 82.54; H, 9.81. $C_{14}H_{20}O$ requires C, 82.35; H, 9.80%).

4-iso*Propyl-6-methoxytetralone*-1 (I): (*i*) *Oxidation by Chromic Anhydride-acetic Acid Mixture.*—1-*iso*Propyl-7-methoxytetralin (13.06 g., 0.064 *M*) in glacial acetic acid (128 c.c.) was placed in a 500 c.c. 3-necked flask fitted with a dropping funnel and a Hershberg stirrer. This was cooled to about 8-10° and chromic anhydride (A.R., 19.2 g., 0.192 *M*), dissolved in water (24 c.c.) and diluted with acetic acid (54 c.c.), was slowly let in with stirring; after addition of the first few c.c., the temperature was rapidly brought down to 0° and the addition continued at that temperature. After the addition (30 minutes) the dark red reaction mixture was allowed to stand at 0° overnight (12-15 hours). This was diluted with water (500 c.c.) and extracted with ether (60 c.c. × 5). The combined ether extracts were washed with brine (15 c.c. × 3) and the solvent (ether and acetic acid) was removed under reduced pressure (water pump) from a water-bath. To the residue some benzene (20 c.c.) was added, which was distilled off to remove traces of moisture. Fractionation of the resulting product furnished the ketone as a pale yellow, somewhat viscous liquid, b.p. 145-50°/0.7 mm, η_D^{26} 1.5630, yield 10.45 g. (75%).

(*ii*) *Oxidation by Sodium Dichromate-acetic acid-benzene Mixture.*—A mixture of 1-*iso*propyl-7-methoxytetralin (20.4 g., 0.1 *M*) and crystalline sodium dichromate (60 g., 0.2 *M*) in glacial acetic acid (300 c.c.) and thiophene-free dry benzene (150 c.c.) was stirred at 25° for 22 hours. Ethanol (25 c.c.) was added towards the end and the stirring continued for 15 minutes more. The reddish green reaction mixture was diluted with water (850 c.c.) and extracted with benzene-ether mixture (1:1, 100 c.c. × 5) and worked up as above to yield the tetralone as a pale yellow, viscous liquid: b.p. 145-47°/0.7 mm, η_D^{27} 1.5620, yield 17.5-18.5 g. (80-85%).

The tetralone, as obtained by method (*i*) or (*ii*), could not be rendered colorless by refractionation. However, the yellow impurity due to the presence of a volatile chromium complex could be best eliminated by filtering the tetralone (one part in one part of dry benzene) through two parts by weight of activated alumina (basic/I, 15 × 4 cm) followed by elution with benzene, when the impurity was strongly adsorbed at the top of the column as a green band. Removal of the solvent from the effluent and fractionation of the residue furnished a colorless liquid, b.p. 140-42°/0.6 mm, η_D^{26} 1.5630, d_4^{26} 1.093, M_D 64.04 (calc. 62.70, EM_D 1.31, $E\Sigma_D$ 0.61); λ_{max}^{EtOH} 276 mμ (ε, 15500). (Found: C, 77.21; H, 8.15. $C_{14}H_{18}O_2$ requires C, 77.06; H, 8.26%).

The 2 : 4-*dinitrophenylhydrazone*, prepared by the sulphuric acid method, was obtained in a quantitative yield. On two crystallisations from glacial acetic acid it separated as dark red small plates, m.p. 202-202.5°. (Found : N, 13.56. $C_{26}H_{22}O_5N_4$ requires N, 14.07%).

The *semicarbazone* (pyridine method) after two crystallisations from dilute ethanol came out as a white crystalline powder, m.p. 163°. (Found : N, 15.27. $C_{15}H_{21}O_2N_3$ requires N, 15.61 %).

(*iii*) *Oxidation by Hydrogen Peroxide.*—1-*iso*Propyl-7-methoxytetralin (2.04 g., 0.01 *M*) in acetone (20 c.c.) was treated with hydrogen peroxide (20-25%, 6.8 c.c., 0.04 *M*) in presence of vanadium pentoxide catalyst (prepared from V_2O_5 10 mg., H_2O_2 20-25%, 0.1 c.c. and acetone 2 c.c) under stirring at laboratory temperature (25°) for 24 hours. The reaction mixture was finally refluxed for 1 hour, when the colour changed from brownish red to reddish green. The solvent was distilled off and the aqueous phase together with the heavy liquid at bottom after cooling was extracted with ether-benzene mixture (1 : 1 ; 20 c.c. × 4). Removal of the solvents from the combined extracts and fractionation of the residue gave a low boiling fore-run (b.p. 108-110°/0.4 mm, η_D^{27} 1.5430, 0.8 g.) apparently consisting mostly of the unoxidised material and a second fraction (b.p. 128-30°/0.4 mm., η_D^{27} 1.5550, 0.4 g., 19%) of the required tetralone (impure), as identified by its 2 : 4-dinitrophenylhydrazone.

One of us (G.S.K.R.) is thankful to the Government of India for the award of a senior research scholarship.

Department of Organic Chemistry,
Indian Institute of Science,
Bangalore-3.

Received September 20, 1956.

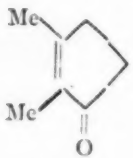
[Jour. Indian Chem Soc., Vol. 34, No. 4, 1957]

ORGANIC REACTIONS WITH POLYPHOSPHORIC ACID. PART V. INTRAMOLECULAR ACYLATION WITH LACTONES: *cyclo*PENTENONES FROM δ-LACTONES

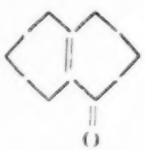
By Sukh Dev and Charanjit Rai

Intramolecular acylation of lactones to yield *cyclo*pentenones in the presence of polyphosphoric acid has been extended to δ-lactones. Based on this, convenient, possibly general, routes to bi*cyclo*-[o:3:3]-octane and bi*cyclo*-[o:3:4]-nonane systems have been described. The reaction has been discussed from the mechanistic point of view.

Various δ-lactones have been converted into the corresponding *cyclo*pentenones by the P_2O_5 method (Frank and Pierle, *J. Amer. Chem. Soc.*, 1951, **73**, 724 ; Ansell and Hey, *J. Chem. Soc.*, 1950, 2875), but the yields have been rather unsatisfactory. Since polyphosphoric acid (PPA) has been shown (Rai and Sukh Dev, this *Journal*, 1957, **34**, 178) to be capable of yielding *cyclo*pentenones from γ-lactones in excellent yields, the method has been extended to δ-lactones. It has been thus possible to synthesise 2:3-dimethyl*cyclo*penten-1-one (I), bi*cyclo*-[o:3:3]-Δ^7-octen-1-one (II) and bi*cyclo*-[o:3:4]-Δ^8-nonen-1-one (III) in very good yields.



(I)



(II)

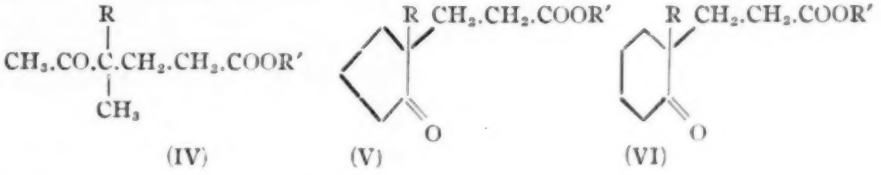
(III)

The general method of synthesis consists in the preparation of a δ-oxo-carboxylic acid, preferably by a Michael addition to a β-keto-ester, followed by hydrolysis; the δ oxo-carboxylic acid is next reduced to yield a δ-lactone, which on intramolecular acylation in the presence of PPA furnishes the *cyclo*pentenone. The method is capable of general extension.

δ-Oxo-carboxylic Acids.—The Michael addition of ethyl methylacetoacetate to ethyl acrylate smoothly furnished ethyl α-methyl-α-acetylglutarate (IVa) in an excellent yield ; its preparation was previously reported by Wislicenus and Limpach (*Annalen*, 1878, **192**, 128) who effected the condensation of ethyl methylacetoacetate with ethyl β-iodopropionate. Ketonic hydrolysis of the product afforded the required γ methyl-δ-oxo-*n*-caproic acid (IVb).

Condensation of ethyl *cyclo*pentanone-2-carboxylate with ethyl β-chloro- or β-bromo-propionate gave ethyl *cyclo*pentanone-2-carboxylate-2-β-propionate (Va) (Cook and Linstead, *J. Chem. Soc.*, 1934, 953) ; this was, however, far more conveniently obtained by the Michael addition of ethyl *cyclo*pentanone carboxylate to ethyl acrylate. It was observed that when the Michael reaction was carried out in the presence of

sodium ethoxide, ring-fission occurred, affording ethyl γ-carbethoxysuberate in 90% yield ; however, when the addition was catalysed by potassium *tert.*-butoxide (Sukh Dev, *Science & Culture*, 1950, **16**, 31) no cleavage of the primary reaction product (Va) occurred. Hydrolysis of (Va) with dilute hydrochloric acid furnished the requisite *cyclo*pentanone-2-β-propionic acid (Vb).

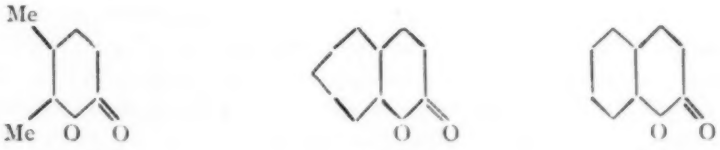


(IV) (V) (VI)

[a : R = COOEt ; R′ = Et]
[b : R = R′ = H]

Similarly (VIa) (cf. Haworth and Mavin, *J. Chem. Soc.*, 1933, 1012) was readily obtained by the interaction of ethyl *cyclo*hexanone-2-carboxylate and ethyl acrylate in the presence of potassium *tert.*-butoxide ; hydrolysis afforded (VIb) in 85% yield.

δ-Lactones.—The δ-lactones (VII, VIII and IX) were prepared by the reduction of the corresponding δ-oxo-carboxylic acids, followed by acidification. The reduction was effected quite smoothly either by the Raney-nickel alloy-alkali method (Schwenk *et al.*, *J. Org. Chem.*, 1944, **9**, 175) or by the sodium borohydride method (Chaikin and Brown, *J. Amer. Chem. Soc.*, 1949, **71**, 122).



(VII) (VIII) (IX)

From a consideration of molecular models it appears that only *cis-cyclo*pentanol-2-β-propionic acid can readily lactonise to (VIII) ; this would indicate the γδ-*cyclo*pentano-δ-valerolactone (VIII), prepared by the procedures described in this communication, should consist essentially of the *cis*-isomer. This conclusion appears to be supported by the fact that whereas both (VII) and (IX) could be prepared in 90% yields by the $NaBH_4$ method, *cyclo*pentanone-2-β-propionic acid (Vb) affords the desired lactone (VIII) in only 50% yield.

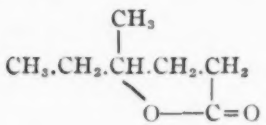
The preparation of γδ-*cyclo*hexano-δ-valerolactone (IX) by different methods has been previously described in the literature (Nenitzescu and Przemetzky, *Ber.*, 1941, **74**, 676 ; Frank and Pierle, *loc. cit.* ; cf. Mathieson, *J. Chem. Soc.*, 1951, 177). Just like the present preparation, these products should be mixtures of *cis*- and *trans*-isomers.

cyclo*Pentenones.*—The δ-lactones (VII, VIII, IX) on treatment with PPA furnished the corresponding *cyclo*pentenones (I, II, III). It has been found that for each lactone there is an optimum set of conditions for the PPA reaction. The lowest temperature

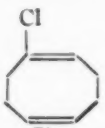
at which the reaction proceeded with a reasonable speed, was always selected for determining the optimum time for the reaction ; at higher temperatures the decomposition of the *cyclo*pentenone became considerable.

γδ-Dimethyl-δ-valerolactone (VII), when treated with PPA at 97° for 4 hours, afforded the maximum yield (80%) of 2 : 3-dimethyl-Δ^2-*cyclo*penten-1-one (I) ; the reaction was exceedingly slow at 80°. Frank *et al.* (*J. Amer. Chem. Soc.*, 1948, **70**, 1379) have reported its preparation from γ-methyl-γ-ethylbutyrolactone (X) by the P_2O_5 method in a very poor yield. It is clear from the extinction coefficient of their product (vide Experimental) that their sample of the *cyclo*pentenone was impure.

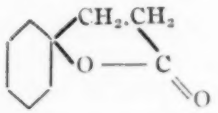
γδ-*cyclo*Pentano-δ-valerolactone (VIII) underwent intramolecular acylation smoothly even at 60° and after 4½ hours of treatment furnished bi*cyclo*-[0 : 3 : 3]-Δ^7-octen-1-one (II) in 92% yield. This compound has been synthesised recently by Cope and Schmitz (*ibid.*, 1950, **72**, 3056) from 2 : 5-dichloro-$\Delta^{1:5}$-*cyclo*octadiene (XI).



(X)



(XI)



(XII)

The conversion of γδ-*cyclo*hexano-δ-valerolactone (IX) to 4 : 5 : 6 : 7-tetrahydroindan-1-one (III) was found to be incomplete under a variety of conditions. At temperatures higher than 80°, the decomposition of the ketone was considerable. Table I records the results of a series of experiments conducted at 80° ± 2°. It is clear from these data that though the conversion to the ketone increases with the time of heating, the overall yield of (III), based on the lactone, falls due to the considerable loss of the material as a result of prolonged heating. Frank and Pierle (*loc. cit.*) carried out the conversion of the lactone (IX) to the tetrahydroindanone (III) by the P_2O_5 method, and reported a yield of 13%. Mathieson (*loc. cit.*) obtained the ketone (III) in a yield of 16% by the P_2O_5-benzene method, and in a yield of 7.5% by the zinc chloride-acetic anhydride method from the spirolactone (XII).

TABLE I

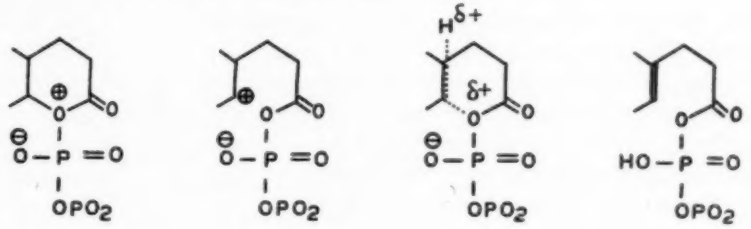
Intramolecular acylation of (IX).

No.	Time *	n_D^{30}.	Yield ‡.	Ketone content.	Absolute yield of the ketone based on the lactone.
1	1 hr.	1.5078	0.70 g.	50.43%	51.9%
2	2	1.5125	0 62	67.89	61.9
3	3	1.5150	0.62	74.33	67.8
4	4	1.5160	0.60	76.17	67.2

* Time for which the reaction was carried out at 80° ± 2°.

‡ Yield of the distillable material (b.p. 130-150°/13 mm) from a PPA reaction using 0.005 *M* of the lactone.

It has been suggested (Johnson and Peterson, *J. Amer. Chem. Soc.*, 1945, **67**, 1366 ; Frank and Pierle, *loc. cit.*) that the intramolecular acylation of lactones proceeds *via* the corresponding unsaturated acid. The lacto-enolic tautomerism is now well recognised (Linstead and Rydon, *J. Chem. Soc.*, 1933, 580 ; Boorman and Linstead, *ibid.*, 1935, 258 ; Johnson, Petersen and Schneider, *J. Amer. Chem. Soc.*, 1947, **69**, 74 ; Mathieson, *loc. cit.*). It appears feasible to consider that in the PPA-catalysed reactions (Sukh Dev, this *Journal*, 1957, **34**, 169) of this type the first step should be the rapid establishment of the reversible equilibrium of the lactone and P_2O_5 with the complex (A)*. This, either by a two-step process passing through (B), or by a concerted mechanism with the transition state (C), should yield the intermediate (D) after taking up the ejected proton †. The intermediate (D) then cyclises through the usual oxo-carbonium ion to provide the cyclic unsaturated ketone.

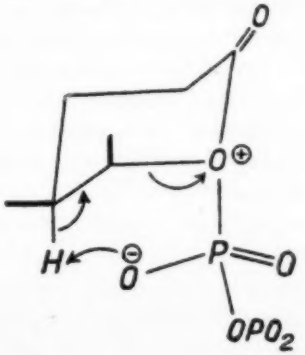


(A) (B) (C) (D)

The formation of the intermediate (D) will be the first rate-determining step on which will be superimposed the rate of ionisation of (D) to give the observed rate of the conversion of the lactone to the ketone. If the formation of (D) passes through (C), the two *cis-trans*-isomers of, say, the lactone (IX), should react at different rates due to the preferred anti-geometry of the transition state ; and since from both isomers (D) will be the same, the observed rate of the reaction can be utilised to possibly distinguish between the two mechanisms. It is hoped to continue the work on these lines.

*In these formulae only a δ-lactone has been depicted ; the same will hold good for a γ-lactone.

† A possible transition state transferring the proton intramolecularly can be :



EXPERIMENTAL

Melting and boiling points are uncorrected. The spectra were measured in 95% ethanolic solution on a Beckman DU spectrophotometer.

2:3-*Dimethylcyclopenten-1-one* (I)

Ethyl α-Methyl-α-acetylglutarate (IVa).—To a solution of potassium (0.1 g.) in *tert.*-butanol (15 c.c.), contained in a 3-necked flask carrying a Hershberg stirrer, a dropping funnel, a thermometer and an outlet tube connected to a guard-tube (SiO_2-gel), ethyl methylacetoacetate (18.0 g., 0.125 *M*) was added in one lot; *tert.*-BuOH (10 c.c.) was used for washing in the last traces of the keto-ester. To the above stirred mixture, ethyl acrylate (16.65 g., 0.15 *M*) was let in dropwise at a rate that the temperature did not go beyond 30° (when the reaction temperature touched 30°, the flask was cooled externally with tap water and the contents maintained at 25-30°); this required (*ca.*) 15 minutes. The reaction mixture was allowed to stand at room temperature (22-25°) for 15 hours. The light orange-coloured product was acidified with glacial acetic acid (2 c.c.) and the resulting pale yellow solution diluted with benzene (50 c.c.), washed with brine (50 c.c. × 2) and dried (Na_2SO_4). The solvent was flashed off (column) and the residue fractionated to give the required product as a colorless liquid, b.p. 114-15°/0.6 mm, 132°/2 mm, η_D^{24} 1.4410, yield 27.5 g. (90%). $FeCl_3$ test was negative (Wislicenus and Limpach, *loc.cit.*, record b.p. 280-81°). (Found: C, 59.4; H, 7.9. Calc. for $C_{12}H_{20}O_5$: C, 59.0; H, 8.2%).

γ-Methyl-δ-oxo-n-caproic Acid (IVb).—A mixture of the above condensation product (24.5 g.), HCl (C.P., 50 c.c.) and water (25 c.c.) was gently refluxed in an oil-bath (135-40°) for 24 hours. The aqueous HCl was then distilled off under reduced pressure (water-pump) from a steam-bath and the residue fractionated to provide: (*a*) fore-run, b.p. 85°-125°/1.2 mm, yield 1.5 g. and (*b*) the required keto-acid (IVb), b.p. 125-26°/1.2 mm, η_D^{24} 1.4460, yield 11.8 g. (82%). (Found: C, 58.2; H, 8.4. $C_7H_{12}O_3$ requires C, 58.3; H, 8.3%).

γδ-Dimethyl-δ-valerolactone (VII): (*i*) *By the Raney-nickel alloy-alkali Method.*—The keto-acid (7.2 g., 0.05 *M*) was dissolved in aqueous NaOH (25 g. in 150 c.c. of water) and the resulting solution was stirred and treated as such with the Ni-Al alloy (-40 mesh; 12 g.) in small portions during 2 hours; excessive foaming was avoided. The reaction mixture was next stirred and heated at (*ca.*) 80° for another 4 hours. After cooling, the solution was filtered to remove the Raney-nickel, which was washed well with water (*ca.* 75 c.c.). The combined filtrate and washings were poured cautiously into H_2SO_4 (C.P., 60 c.c. and water 120 c.c., mixed before use). The hot mixture was left aside for 4 hours, saturated with sodium chloride and extracted with with ether (35 c.c. × 6), washed with brine (35 c.c. × 2) and dried (Na_2SO_4). The solvent was distilled off and the residue fractionated to furnish the lactone as a colorless liquid, b.p. 91°/2 mm, η_D^{24} 1.4535, yield 4.8 g. (75%).

(*ii*) *By Sodium Borohydride Reduction.*—The keto-acid (3.6 g., 0.025 *M*), dissolved in water (20 c.c.) containing sodium bicarbonate (2.5 g., 0.03 *M*), was cooled in an ice-bath and sodium borohydride (0.47 g., 0.0125 *M*) added in one lot with swirling.

After shaking at the ice-temperature for 5 minutes, it was left aside at room temperature (25°) for 4 hours. The mixture was carefully acidified with HCl (conc.) to p_H 2 and left aside overnight (15 hrs.). The almost clear solution was saturated with NaCl, when an oil separated, which was taken up in ether (10 c.c. × 6) and worked up as above to yield the lactone, b.p. 91°/2 mm, $\eta_D^{25.5}$ 1.4535, yield 3.1 g. (97%).

A refractionated (central cut) sample had b.p. 85°/1.5 mm, $\eta_D^{25.5}$ 1.4520, $d_4^{25.5}$ 1.013, M_D 34.10 (calc. 33.99). (Found: C, 65.3; H, 9.4. $C_7H_{12}O_2$ requires C, 65.6; H, 9.4%).

2:3-*Dimethyl*-Δ^2-cyclo*penten*-1-*one*(I).—To PPA (from P_2O_5, 7 g. and 85% syrupy phosphoric acid, 3 c.c. Sukh Dev, this *Journal*, 1955, **32**, 262), contained in a test-tube (6″ × 1″) and maintained at 97° (immersed in a boiling water-bath), the above lactone (0.64 g., 0.005*M*) was added in one lot, mixed well with a glass rod and the resulting pale coloured mixture heated at 97° for 4½ hours under dry conditions. The mixture was well mixed thrice during this period of heating by tilting the test-tube so that its contents covered the walls and then flowed back. The red-brown product, obtained at the end of the above heating period, was diluted, with cooling, with ice-water to (*ca.*) 40 c.c. and to this ammonium sulphate (20 g.) was added and the whole extracted continuously with petroleum ether for 30 hours. From the extract the solvent was fractionated off and the residue distilled to furnish the ketone as a colorless liquid, b.p. 91-92°/22 mm, η_D^{30} 1.4848, yield 0.44 g. (80%).

With larger quantities, the reaction was best carried out in a 3-necked flask with a Hershberg stirrer; the reaction mixture was stirred vigorously for two minutes to effect mixing and then the reaction continued without stirring.

An analytical sample had b.p. 80°/10 mm, $\eta_D^{25.5}$ 1.4855, $d_4^{25.5}$ 0.9677, M_D 32.61 calc. for $C_7H_{10}O$ $\overline{|1|}$, 31.88; $E\Sigma_D$ 0.66); λ_{max} 234 mμ (ϵ, 13660). (Frank *et al.*, *loc. cit.*, report b.p. 90-92°/25 mm, η_D^{20} 1.4830, λ_{max} 235 mμ, log ϵ 3.04).

The 2:4-*dinitrophenylhydrazone* (HCl method) (crude m.p. 214-15°) was obtained as minute red prisms from glacial acetic acid, m.p. 226-27° (decomp.). (Found: N, 19.4. $C_{13}H_{14}O_4N_4$ requires N, 19.3%).

*Bi*cyclo-[0:3:3]-Δ^7-*octen* 1-*one* (II)

Ethyl cyclo*Pentanone-2-carboxylate-2-β-propionate* (Va): (*i*) *By Michael Addition.*—Ethyl acrylate (16.65 g., 0.15 *M*) was allowed to react with ethyl *cyclo*pentanone-2-carboxylate (19.5 g., 0.125 *M*) in the presence of potassium *tert.*-butoxide (from potassium 0.1 g.) exactly as described for (IVa). The reaction was more exothermic and the contents had to be cooled with water at (*ca.*) 15° (instead of tap water) to maintain the temperature between 25° and 30° and finish the addition of the ethyl acrylate within ½ hour. The reddish orange reaction mixture was worked up as described above to provide (Va) as a colorless oil, b.p 140-42°/1 mm, $\eta_D^{25.5}$ 1.4560, yield 29.3 g. (91.5 %).

When in the above reaction, potassium *tert.*-butoxide was replaced by sodium ethoxide (from sodium 0.1 g., alcohol 20 c.c.) the product obtained (from 0.125 *M* of the keto-ester) had b.p. 185-88°/3 mm, η_D^{25} 1.4400, yield 27 g. (89.4%) and was identified as *ethyl* γ-*carbethoxysuberate* by hydrolysis (2 parts of conc. HCl; refluxed for

6 hours) to the corresponding *tricarboxylic acid*, m.p. 111° (white prisms from ethyl acetate) (Cook and Linstead, *loc. cit.*, report b.p. 186°/9 mm for the ester and m.p. 111° for the acid).

(*ii*) *By Condensation with Ethyl β-Halopropionate.*—Ethyl β-bromopropionate (199 g., 1.1*M*) and the sodio derivative of ethyl *cyclo*pentanone carboxylate (from sodium 23 g., 1 g. atom and keto-ester 156 g., 1 *M*) were condensed in toluene (500 c.c.), exactly as described by Sukh Dev (this *Journal*, 1953, **30**, 817); b.p. 140°/1 mm, η_D^{25} 1.4570, yield 210 g. (82%) (Cook and Linstead, *loc. cit.*, report b.p. 189°/18 mm, $\eta_D^{19.4}$ 1.4563, yield 75% from ethyl β-chloropropionate).

When in this reaction ethyl β-chloropropionate replaced the bromo-ester, the yield was almost the same.

cyclo*Pentanone-2-β-propionic Acid* (Vb).—The above condensation product (29 g.) was hydrolysed with a mixture of HCl (C.P., 58 c.c.) and water (29 c.c.), as detailed for (IVb) to afford the keto-acid: b.p. 143-44°/0.6 mm; the distillate slowly solidified, m.p. 35-38°, yield 15.8 g. (90%) (Cook and Linstead, *loc. cit.*, report m.p. 37°).

γδ-cyclo*Pentano-δ-valerolactone* (VIII): (*i*) *By the Raney-nickel alloy-alkali Method.*—A solution of the keto-acid (24.96 g., 0.16 *M*) in aqueous NaOH (75 g. in 450 c.c. of water) was reduced with the alloy (37 g.) by following closely the procedure described for the preparation of (VII). On fractionation the lactone was obtained as a colorless liquid, b.p. 107-109°/1.5 mm, η_D^{24} 1.4835, yield 12 g. (53.6%).

In one experiment with half the quantities of the materials, the ethereal extract was extracted with saturated aqueous $NaHCO_3$ to obtain the acidic and neutral portions. The neutral portion on working up afforded the lactone (b.p. 100-101°/1 mm, η_D^{24} 1.4835, yield 3.5 g.) leaving practically no distillation residue. A similar distillation of the acidic part yielded the same lactone (2.5 g., same physical constants) and a polymeric residue (*ca.* 4 g.) remained.

A refractionated (central cut) sample had b.p. 109°/1.5 mm, $\eta_D^{25.5}$ 1.4825, $d_4^{25.5}$ 1.101, M_D 36.28 (calc. 36.41). (Found: C, 68.9; H, 8.6. $C_8H_{12}O_2$ requires C, 68.6; H, 8.6 %).

(*ii*) *By Sodium Borohydride Method.*—The keto-acid (3.9 g., 0.025 *M*) was reduced by following the procedure detailed for the lactone (VII). In this case, removal of the solvent from the ether extract gave a viscous product, which was distilled to collect the material boiling up to 130°/1 mm (yield 2.7 g.); a polymeric residue was left. Refractionation of the crude distillate afforded the required lactone, b.p. 122°/2.5 mm, η_D^{24} 1.4820, yield 1.6 g. (45.7%).

Bicyclo-[0:3:3]-Δ^7-*octen*-1-*one* (II).—The above lactone (0.7 g., 0.005 *M*) was treated with PPA in the manner described above for the ketone (I), except that the reaction was conducted at 60° ± 2° for 4½ hours. On working up the reddish brown reaction mixture in the same manner, the bi*cyclo*-ketone (II) was obtained as a colorless mobile liquid, b.p. 114-15°/13 mm. η_D^{29} 1.5155, yield 0.58 g. (91.8 %).

A refractionated sample had b.p. 110°/10 mm, m.p. 8-10°, $\eta_D^{25.5}$ 1.5190, $d_4^{25.5}$ 1.053, M_D 35.16 (calc. for $C_8H_{10}O$ $\overline{|1|}$ 34.30; $E\,\Sigma_D$ 0.70); λ_{max} 240 mμ (ε, 11880); *semicarbazone* (by pyridine method) was obtained in white minute silky needles (dilute pyridine),

m.p. 231-32° (decomp.) (Cope and Schmitz, *loc. cit.*, report b.p. 62°/0.9 mm, η_D^{25} 1.5202, d_4^{25} 1.0534, m p. 17.2-19° ; $\lambda_{max}^{cyclohexane}$ 234mμ, ε 11280 ; semicarbazone m.p 230-32°).

The 2 : 4-*dinitrophenylhydrazone* (HCl method) (crude m.p. 220-22°) was crystallised first from acetic acid and then from xylene to furnish dark red flat needles, m.p. 221-22°. (Found : N, 18.3. $C_{14}H_{14}O_4N_4$ requires N, 18.3%).

Bicyclo-[0 : 3 : 4]-Δ^8-*nonen*-1-*one* (III)

Ethyl cyclo*Hexanone*-2-*carboxylate*-2-*β*-*propionate* (VIa).—The addition of ethyl acrylate (16.65 g., 0.15 *M*) to ethyl *cyclo*hexanone-2-carboxylate (21.25 g., 0.125 *M*) was carried out in the manner described for the analogue (IVa). The reaction was less exothermic as compared to the corresponding case of ethyl *cyclo*pentanone carboxylate. On working up the deep orange-red reaction mixture, the required product (VIa) was obtained as a colorless oil, b.p. 148-49°/0.9 mm, η_D^{23} 1.4630, yield 91.2% (Haworth and Mavin, *loc. cit.*, record b.p. 199-202°/15 mm).

When the above reaction was conducted in the presence of sodium ethoxide instead of potassium *tert.*-butoxide, no ring-fission occurred, in contrast to the behaviour of the 5-membered analogue.

cyclo*Hexanone*-2-*β*-*propionic Acid* (VIb).—The above ester (30 g.), HCl (C.P., 60 c.c.) and water (30 c.c.) were refluxed for 24 hours and then freed of the aqueous HCl etc. under suction from a steam-bath. The cold residue was taken up in aqueous NaOH (6 g. in 60 c.c. of water), washed once with ether (50 c.c.) and the alkaline solution acidified (*p*H 2), with cooling, with syrupy phosphoric acid. The acid was taken up in ether (50 c.c. × 3), washed with brine (50 c.c. × 2) and dried (Na_2SO_4). The solvent was flashed off and the residue fractionated, b.p. 153°/0.5 mm ; it solidified as it distilled, m.p. 58-62°, yield 16 g. (84.6%) ; this was used as such for the next step (Haworth and Mavin, *loc. cit.*, report b.p. 155-60°/0.2 mm, m.p. 65-66°).

When the procedure described for (IVb) was followed instead of the above, the yield of the distilled acid fell (75-79%) due to the formation of a lower boiling liquid (b.p. 110-15°/0.6 mm, $\eta_D^{22.5}$ 1.4650) ; this immediately decolorised Br_2 in CCl_4 and may be the enol-lactone (?).

γδ-cyclo*Hexano*-δ-*valerolactone* (IX): (*i*) *By the Raney-nickel alloy-alkali Method.*—The keto-acid (23 8 g., 0.14 *M*) in aqueous NaOH (75 g. in 450 c.c. of water) was reduced with the alloy (37 g.) as described for the lactone (VII) : b.p. 115-18°/2 mm, η_D^{28} 1.4790, yield 15.8 g. (70%).

An analytical sample had b.p. 110-12°/1.5 mm, $\eta_D^{25.5}$ 1.4815, $d_4^{25.5}$ 1.072, M_D 40.93 (calc. 41.03) (Frank and Pierle, *loc. cit.*, report b.p. 110°/1 mm, η_D^{20} 1.4912).

(*ii*) *By Sodium Borohydride Method.*—The keto-acid (4.25 g., 0.025 *M*) was reduced and lactonised by following the procedure described for the preparation of (VII) : b.p. 142°/5 mm, yield 3.46 g. (90%).

4 : 5 : 6 : 7-*Tetrahydroindan*-1-*one* (III).—The above lactone (0.77 g., 0.005 *M*) was treated with PPA at 80° ± 2° by following the procedure detailed for the ketone (I). The data recorded in Table I was obtained by carrying out this reaction for different periods of time. The ketone content of the distillate was measured as follows :

To a weighed sample (*ca.* 0.15 g.) of the distillate, contained in a conical flask, 40 c.c. of the 2 : 4-dinitrophenylhydrazine reagent (prepared by dissolving 4 g. of the solid reagent in 40 c.c. of C.P. H_2SO_4 and 60 c.c. of water and diluting to 400 c.c. with 95% ethanol and filtering) was added. The mixture was heated to boiling and boiled for 1 minute and then left aside as such at room temperature for 1½ hours. After chilling to -5° for 10 minutes, the precipitated derivative was collected on a tared sintered glass funnel under suction. The precipitate was washed with dilute alcohol (1 : 1 ; 50 c.c.) and dried at 75° for 15 hours. A check with a pure specimen (*vide infra*) of (III) gave the ketone content of 99.36%.

The samples of 2 : 4-*dinitrophenylhydrazone*, obtained in the above estimations, were combined (m.p. 218-20°) and recrystallised twice from xylene to provide dark red leaflets, m.p. 229-30°, unaltered on admixture with an authentic specimen.

It was not possible to separate completely the ketone (III) from the lactone (IX) by fractionation. The following method was adopted to effect the separation : The distillate (4.0 g., ketone content 65%), dissolved in *n*-hexane (30 c.c.), was stirred vigorously for 2 hours at room temperature with aqueous KOH (1 g. in 40 c.c. of water). The hexane layer was separated and the dark red aqueous phase extracted with hexane (15 c.c. × 2). After washing the extracts with brine (15 c.c. × 2) and drying (Na_2SO_4) the solvent was removed (column) and the residue fractionated : b.p. 127-28°/13 mm, $\eta_D^{26.5}$ 1.5225, yield 2.4 g. (92%). A refractionated sample had b.p. 123°/10 mm, $\eta_D^{25.5}$ 1.5225, $d_4^{25.5}$ 1.044, M_D 39.76 (calc. for $C_9H_{12}O$ $\overline{|}$ 38.92 ; $E\Sigma_D$ 0.62) ; λ_{max} 237 mμ (ε, 13400) (Sukh Dev, this *Journal*, 1955, **32**, 264 : b.p. 141°/30 mm, η_D^{26} 1.5225 ; λ_{max} 237 mμ, log ε 4.11).

DEPARTMENT OF ORGANIC CHEMISTRY,
INDIAN INSTITUTE OF SCIENCE,
BANGALORE-3.

Received September 20, 1956.

Jour. Indian Chem Soc., Vol. 34, No. 4, 1957]

STUDIES IN THE CHEMISTRY OF TELLURIUM. PART II. THE ELECTRODIC BEHAVIOUR OF TELLURIUM IN BUFFER SOLUTIONS OF VARYING *p*H

By I. M. Issa, H. Khalifa and S. A. Awad

Tellurium electrodes, prepared from the powdered metal or by electrodeposition and then subjected to the alternate action of hydrogen and high vacuum or prepared by sublimation in vacuum, set up potentials in oxygen-free buffer solutions, which coincide with the thermodynamic potentials of the Te/TeO_2 system. They differ thus from the potentials set by the massive electrodes or electrodes prepared by electrodeposition in aerated solutions which are more positive by ~ 160 mv. This excess potential corresponds to 2/15 of the electrode surface being covered with oxygen doublets.

In a previous investigation two of us studied the applicability of tellurium as indicator electrode in acid-base titrations (Tourky, Issa and Awad, *Chim. Anal.*, 1955, **37**, 367). For this purpose the behaviour of tellurium electrodes, prepared either from tellurium rods or by electrodeposition, was investigated in buffer solutions of p_H 1-12. Tellurium rods or tellurium electrodes, prepared by electrodeposition from weakly acid solutions of TeO_2 ($p_H \sim 3$), showed a p_H-potential relationship consisting of two linear portions covering the p_H ranges 1-5 and 7-12. Electrodes prepared by electrodeposition from fairly acid solutions (2*N*-HCl) showed, on the other hand, a linear plot within the p_H range 3-11. Extrapolation of the linear portions to $p_H = 0$ yielded in case of the former electrodes E'_0 values which within the p_H range 1-5 amount to 0.53 volt, and within the p_H range 7-12 to 0.69 volt. The E'_0 values, obtained by tellurium electrodes deposited from fairly acid solutions, approached the higher E'_0 value, *i.e.* 0.69 volt.

In this investigation it is aimed to throw some light on the electrode mechanism from a study of the behaviour of the tellurium electrode out of contact with atmospheric oxygen and from its behaviour on cathodic and anodic polarisation.

Experimental

The electrodes studied were obtained from (*a*) the massive or the powderd metal, (*b*) by electrodeposition and (*c*) by sublimation.

(*A*). The massive tellurium electrodes were prepared by the process described previously by Khalifa and Issa (this *Journal*, 1957, **34**, 88) and shown in Fig 1 a.

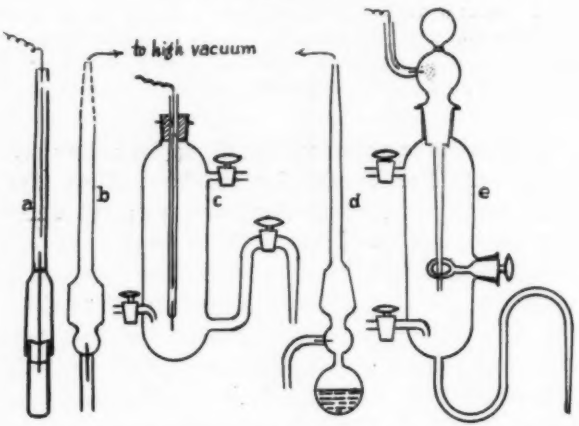
(*B*) *Powdered electrodes.*—The metal powder was obtained by reducing an acid solution of tellurium dioxide with sulphur dioxide. The powder was placed in a small glass cup surrounding platinum wires sealed to glass tubings that could be filled with mercury for maintaining the electrical contact.

(*C*). Electrodes prepared by sublimation of powdered tellurium, after being subjected to the reducing action of hydrogen and high vacuum at 400°.

Cells and Apparatus.—Measurements in air were carried out in an electrode vessel similar to that previously given (Issa *et al.*, *Rec. trav. chim.*, 1955, **74**, 1506). The electrode vessel (c) shown in Fig 1 is used to carry out measurements while bubbling either purified nitrogen or hydrogen through the solution. The vessel (e, Fig. 1) is designed for measuring the potentials of tellurium electrodes out of contact with atmospheric oxygen, and after subjecting them to the alternate action of hydrogen and high vacuum between 200° and 400°. Electrodes subjected to the above treatment were either prepared by electrodeposition or by sublimation.

FIG. 1

Electrode jackets and cells



Electrodeposited electrodes were heated in vacuum at 200° and in hydrogen at 400°. This treatment was followed on account of the tendency of tellurium to volatilise in vacuum at about 320° (Latimer "Oxidation Potentials", Prentice-Hall, N.Y., 1953, p. 86).

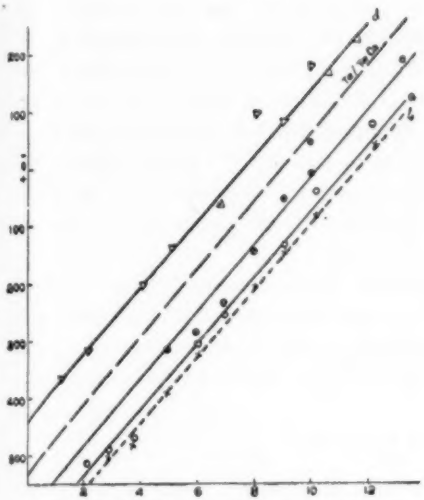
After repeating this process twice, the electrode jacket (b, Fig. 1) was evacuated, left to cool and then separated from the vacuum system by sealing at a narrow constriction. By the aid of a breaking device in the electrode vessel (e, Fig. 1) containing the air-free buffer, the electrode jacket could be completely filled with the solution.

Electrodes prepared by sublimation were obtained by subjecting the powdered metal to the reducing action of hydrogen at 400°, followed by high vacuum at 320°. The metal sublimed and deposited on a platinum wire sealed inside the electrode jacket (d, Fig. 1). Electrical contact in all cases was maintained through mercury and copper wires.

Behaviour of Tellurium Electrodes prepared by Electrodeposition

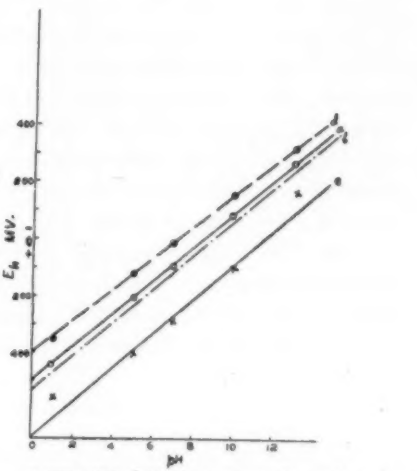
(*a*) *In Air.*—Curves a and b (Fig. 2) represent the potential—p_H plots three hours after immersion for tellurium electrodes prepared from neutral and alkaline tellurate solutions respectively on a platinum substrate. These curves represent a linear relation between p_H and potential within the p_H range 2-12 with the respective slopes, 67 and 58. By extrapolation to zero p_H, E_o values amounting to 650 and 680 mv successively were obtained.

FIG. 2



Electrodeposited electrodes (a) from neutral (b) from alkaline (c) hydrogen bubbling (d) N_2 bubbling

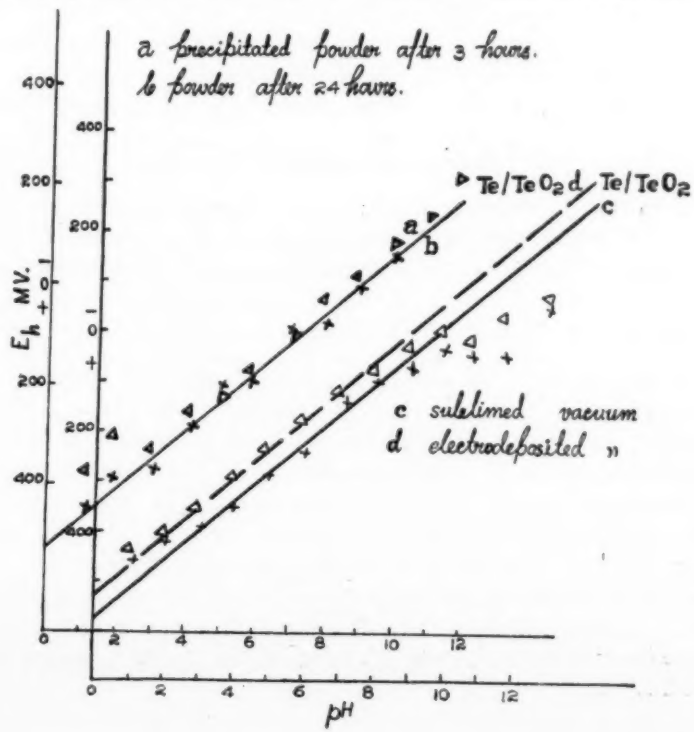
FIG. 3



a) massive (CH_4) b) Te/TeO_2 c) massive after anodic treatment d) massive after cathodic treatment.

FIG. 4

Potential-p_H relation for tellurium electrodes pretreated with hydrogen.



Curves c and d in Fig 2. show the behaviour of electrodeposited electrodes in solutions originally freed from dissolved oxygen by bubbling purified nitrogen or hydrogen through the solution for a period of 30 minutes while the electrodes were immersed in the solution. Both curves are linear and possess slopes of 59 mv. They differ from the curves obtained in aerated solutions in that the potentials set in the latter case are more positive. The potentials initially set in presence of hydrogen are even less positive than those of the Te/TeO_2 system. Thus, by extrapolation to zero p_H, E'_o values amounting to 600 and 400 mv are obtained in case of nitrogen and hydrogen respectively. In both cases the potentials tend to more positive values with time till they reach after prolonged immersion the values obtained in air.

(*b*) *Out of Contact with Air.*—Curve d in Fig. 4 represents the behaviour of the electrodeposited electrodes after subjecting them to the alternate action of hydrogen and high vacuum. The potentials which remain practically constant throughout a period of 24 hours lie on a straight line which coincides with the theoretical ones for the Te/TeO_2 system.

Behaviour of Powdered Electrodes

(*a*) *In Air.*—Curve b in Fig. 4 shows the behaviour of electrodes prepared from the powdered metal. From the results obtained in air it was found that within the p_H range 1-5, the potentials set 3 hours after immersion lie in the region of the Te/TeO_2 system. Above this p_H range the potentials are somewhat more positive than the corresponding thermodynamic values but tend to drift with time to less positive potentials till they approach after 24 hours those of the Te/TeO_2 system.

(*b*) *Out of Contact with Air.*—Powdered electrodes, after being subjected to the alternate action of hydrogen and high vacuum set potentials which, as may be seen from curves a and b in Fig. 4, coincide within the p_H range 1-10 with the thermodynamic values.

Behaviour of Sublimed Electrodes

Curve c in Fig 4 represents the behaviour of tellurium electrodes prepared by sublimation. These electrodes like those subjected to the alternate action of hydrogen and high vacuum set potentials which lie in the region of the thermodynamic values.

Behaviour of Stick Tellurium Electrodes after Cathodic and Anodic Treatment

Curves d and c in Fig. 3 represent the variation of potentials with p_H, set by the massive electrodes after being subjected to cathodic and anodic polarisation at 4×10^{-5} amps/cm^2. In both cases the potentials lie on almost straight lines and yield on extrapolation to $p_H = 0$, E'_o values amounting to 400 and 650 mv in case of cathodically and anodically treated electrodes respectively. The potentials set by the cathodically polarised electrodes are less positive than of the Te/TeO_2 system whereas those set by the anodically polarised electrodes are more positive.

For the sake of comparison, the E'_o values obtained by extrapolating the $E_h - p_H$ plots obtained in air and out of contact with atmospheric oxygen to $p_H = 0$ together with the difference from the thermodynamic E'_o value of the Te/TeO_2 system (0.529 volt) are listed in Table I.

TABLE I

Electrode.	E'_o in presence of air.	Diff from E'_o (thermodynamic).	E'_o out of contact with air.	Diff. from E'_o (thermodynamic)
Deposited from neutral tellurate	650 mv	+120 mv		
Deposited from alkaline tellurate	680	+150		
Deposited from acid tellurite			530 mv (vacuum)	...
			440 (hydrogen)	−90 mv
			600 (nitrogen)	+70
Powdered	530 (p_H 1-5)	...	530 (p_H 2-9)	...
	570 (p_H 7-11)	+40		
Sublimed			530	...
	530 (p_H 1-5)	...	500 (hydrogen)	−30
Massive	600 (p_H 7-12)	+160	400 (cathodic polarisation)	−130
			650 (anodic polarisation)	−120

DISCUSSION

Tellurium is known to afford the oxides TeO_2 and TeO_3. No thermodynamic values are known for the oxide TeO_3, hence we shall limit our discussion to the dioxide. According to Latimer (*loc. cit.*) the thermodynamic E'_o value of the Te/TeO_2 system, as calculated from the free energy change of the reaction:

$$Te + 4\ H_2O + 4e \rightleftharpoons TeO_2 + 4\ OH^-,$$

amounts to 0.529 volt at 25°.

Comparison of the E'_o values in Table I with the thermodynamic one indicates that values approaching the latter are obtained only in case where the electrodes are subjected to the alternate action of hydrogen and high vacuum and when the measurements are taken out of contact with atmospheric oxygen. Under these conditions the electrode behaves as a tellurium-tellurium dioxide electrode. Similar behaviour was observed in the case of electrodes prepared from the powdered metal within the p_H range (1-5) for the potentials set 3 hours after immersion and all over the p_H range after prolonged immersion (24 hours). In presence of air and when the massive electrodes are used, on the other hand, potentials more positive than the thermodynamic ones are obtained. This behaviour is similar to that previously observed by Tourky and Moussa in the case of arsenic and antimony and is most probably due to an oxygen-overvoltage effect (*J. Chem. Soc.*, 1948, 750; 1949, 1297) superimposing the reversible behaviour of the Te/TeO_2 couple. The overvoltage effect results from the presence on the electrode surface of an oxygen film, most probably in the form of doublets. This film is removed by subjecting the electrode to the alternate action of hydrogen and high vacuum, leading to the attainment of the reversible potentials. This view is further substantiated by the behaviour of the powdered electrodes (Tourky *et al.*, *loc. cit.*) and by the effect of the prevailing gaseous atmosphere on the electrode behaviour. On bubbling nitrogen

gas through the solution in which the electrode is immersed, oxygen is removed from the solution and partly from the electrode surface, leading to potentials less positive than the values obtained in air. In case of hydrogen, the gas may be adsorbed at the electrode surface leading to potentials, less positive than the thermodynamic values. The same behaviour is observed on subjecting the electrode to cathodic polarisation.

The origin of the oxygen-overvoltage effect may be explained in the following manner: In tellurium dioxide, like other polyvalent metal oxides, the lattice defects are restricted to oxygen ions (Mott, *Trans. Faraday Soc.*, 1940, **36**, 472). During the oxidation of the metal, thickening of the oxide is not liable to take place. This is because the metal ions are unable to migrate from the metal surface to the oxide gas interface and the oxygen deposited on the electrode surface will remain as oxygen doublets, subjecting the electrode to an oxygen-overvoltage effect.

Based on the findings of Bowden (*Proc. Roy. Soc.*, 1929, **A125**, 445), the oxygen-overvoltage effect superimposing reversible potential of the Te/TeO_2 system and amounting in maximum to 160 mv is sufficient to cover 2/15 of the electrode surface with oxygen doublets. Bowden (*loc.cit.*) found that the quantity of electricity necessary to establish oxygen overvoltage per 100 mv was 11×10^{-6} coulombs. Taking the real area equal to 2-3 times the apparent one, he calculated that this quantity of electricity was sufficient to cover 1/15 of the surface with oxygen doublets. This overvoltage effect was observed in cases of molybdenum and chromium electrodes which exhibited greater tendencies for passivity (Tourky, Issa and Khalifa, *J. Inst. Egypte*, 1956; Issa and Khalifa, this *Journal*, 1956, **33**, 465). In the case of the latter two metals the overvoltage effect was said to be due to the fact that 1/4 and 2/3 of the surface are covered with oxygen doublets respectively.

The authors wish to express their thanks and gratitude to Professor A. Riad Tourky for his help and advice.

CHEMISTRY DEPARTMENT,
FACULTY OF SCIENCE,
CAIRO UNIVERSITY,
GIZA, EGYPT.

Received October 29, 1956.

[Jour. Indian Chem. Soc., Vol. 34, No. 4, 1957]

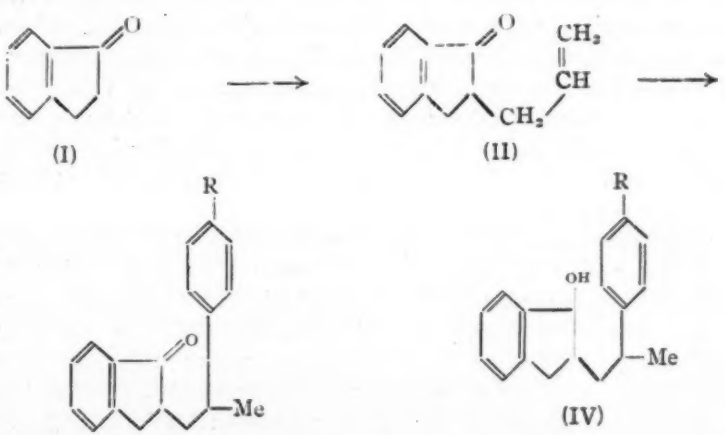
POLYNUCLEAR AROMATIC HYDROCARBONS. PART V. A NEW ROUTE TO 3:4-BENZFLUORENE DERIVATIVES

By O. P. Vig, R. P. Gandhi and (Miss) R. K. Gulati

By an extension of the method of Mukherji *et al.* (*J. Org. Chem.*, 1952, **17**, 1202 ; 1953, **18**, 1499 ; 1954, **19**, 328), syntheses of hitherto-unknown 2-methyl- and 2:4'-dimethyl-3:4-benzfluorenes have been described.

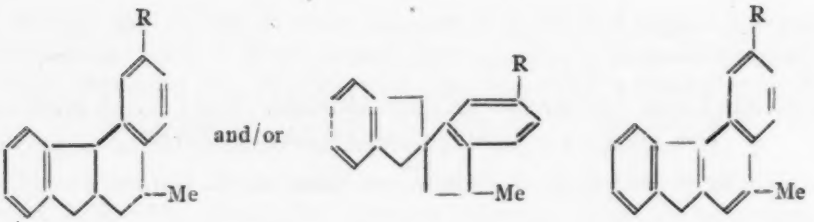
3:4-Benzfluorene ring system, unlike other polynuclear aromatic hydrocarbons, has not been studied so extensively from the standpoint of carcinogenic activity (Bachman *et al.*, *Proc. Roy. Soc.*, 1937, **B 123**, 343, 354). The study of 3:4-benzfluorene and its alkyl derivatives, however, offers some points of interest because of their inhibiting action on the implanted Crokes mouse sarcoma (Haddow and Robinson, *Proc. Roy. Soc.*, 1939, **B 127**, 277, 280). The literature records a few isolated methods for the synthesis of 3:4-benzfluorene derivatives (Cook *et al.*, *J. Chem. Soc.*, 1935, 1913 ; Rapson and Shuttleworth, *ibid.*, 1940, 637 ; Fieser and Joshel, *J. Amer. Chem. Soc.*, 1940, **62**, 957). The present communication reports a new route to the various alkyl derivatives of this tetracyclic aromatic hydrocarbon by adopting a facile variation of the general method of Mukherji *et al.* (*loc.cit.*) for building up multi-ringed hydrocarbon systems.

The starting meterial, 2-allyl-1-indanone (II), was obtained through the interaction of 1-indanone (I) (potassio salt) with allyl iodide in 60% yield. The ketone (II), on being subjected to anhydrous aluminium chloride-catalysed condensation with thiophene-free benzene at 0°-5°, produced 2-[β-methyl-β-(phenyl)-ethyl]-1-indanone (IIIa) in 70% yield. Subsequent reduction of (IIIa) with lithium aluminium hydride in anhydrous ether afforded 2-[β-methyl-β-(phenyl)-ethyl]-1-indanol (IVa) in 90% yield.



(I) (II) (III) (IV)

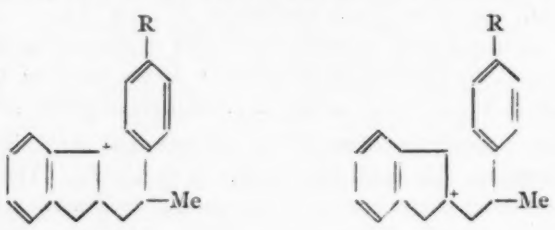
[a: R=H b: R=Me]



(V) (VI) (VII)

[a: R=H]
[b: R=Me]

The carbinol (IVa) was cyclised with concentrated sulphuric acid at 0° in 60% yield to 2-methyl-1:2:10:11-tetrahydro-3:4-benzfluorene (Va) and/or the spiran (VIa). The possible formation of a spiran such as (VIa) can be rationalised by a consideration of the low nucleophilicity of the aromatic system which allows the reaction to proceed in a non-concerted manner (Stork and Burgstahler, *J. Amer. Chem. Soc.*, 1955, **77**, 5068) with the intermediate formation of the more stable carbonium ion.



(A) (B)

But from energetic considerations the carbonium ion (A) should be more stable than (B) because the positive charge in (A) is in mesomerism with the benzene ring. This reduces or excludes the formation of spiran (VIa) under this condition. However, no attempt was made to separate the two (Va) and (VIa) (if any), since on dehydrogenation both were expected to give rise to the same aromatic hydrocarbon (VIIa) so long as the hydrindane moiety in the spiran (VIa) remained symmetrical. Dehydrogenation of the above hydro derivative (Va) and/or (VIa) was effected over 30% Pd--C catalyst in 4 hours at 300°-320° in 65% yield. The resulting hydrocarbon, 2-methyl-3:4-benzfluorene (VIIa) furnished a red picrate.

Similarly anhydrous sulphur-free toluene was allowed to react with 2-allyl-1-indanone (II) in the manner of (IIIa) when the ketone (IIIb) was formed in 90% yield. The *para*-orientation in the product (IIIb) was established by its alkaline permanganate oxidation to a mixture of phthalic acid and terephthalic acid. No trace of *iso*phthalic acid could be detected, indicating exclusive *para*-orientation under these conditions. The ketone (IIIb), on reduction with lithium aluminium hydride, produced the corresponding carbinol, *i.e.* 2-[β-methyl-β-(p-tolyl)-ethyl]-1-indanol (IVb) in 85% yield. The cyclisation of (IVb) with concentrated sulphuric acid at 0° afforded 2:4′-dimethyl-1:2:10:11-tetrahydro-3:4-benzfluorene (Vb) and/or the spiran (VIb), in 65% yield.

The dehydrogenation of the above hydro derivative (Vb and/or VIb) was accomplished over 30% palladium-charcoal catalyst at 300°-320° for 4 hours in 70% yield. The resulting 2 : 4′-dimethyl-3 : 4-benzfluorene was characterised through its reddish brown picrate.

EXPERIMENTAL*

Indanone-1 (I) was prepared from β-phenylpropionic acid, essentially according to the procedure of Johnson and Glenn (*J. Amer. Chem. Soc.*, 1949, **71**, 1092).

2-Allyl-1-indanone (II).—To a cooled solution of potassium (3.8 g.) in *tert.*-butyl alcohol (200 c. c.) (moisture excluded) was added dropwise 1-indanone (12.8 g.) and the mixture left standing overnight. To the orange-coloured solid mass that separated was introduced, gradually and with continual shaking, allyl iodide (18 g.). After waiting for one hour at room temperature, the contents were refluxed for 8 hours and sufficient water was then added to dissolve the potassium iodide formed. The contents were then worked up in the customary manner and the product was obtained as a colorless mobile oil distilling at 140-45°/15 mm. yield 10 g. (60%); η_D^{17} 1.5608. (Found : C, 83.20 ; H, 6.87. $C_{12}H_{12}O$ requires C, 83.69; H, 7.02%).

The 2 : 4-*dinitrophenylhydrazone* derivative after crystallisation from ethyl acetate was obtained as orange-red needles, m.p. 161-62°. (Found : N, 16.3. $C_{18}H_{16}O_4N_4$ requires N, 15.9%).

The *semicarbazone* of the above ketone crystallised from ethanol as colorless needles, m.p. 187-88°. (Found : N, 18.8. $C_{13}H_{15}ON_3$ requires N, 18.33 %).

2-[β-Methyl-β (phenyl)-ethyl]-1-indanone (IIIa).—To anhydrous thiophene-free benzene (100 c.c.) was introduced with vigorous stirring and efficient cooling (0°-5°) a total of 13 g. of anhydrous aluminium chloride and 2-allyl-1-indanone (II : 8 g.) during 80 minutes. The reaction mixture was stirred for an additional 5 hours at 0°-5° and then decomposed with iced HCl and the hydrolysate was ether-extracted. The solvent was flashed off from the united ether-benzene extracts to leave 8 g. (69%) of a light yellow immobile oil which distilled at 197-200°/8 mm, η_D^{17} 1.5862. (Found : C, 85.93 ; H, 6.95. $C_{18}H_{18}O$ requires C, 86.36 ; H, 7.25 %).

The *semicarbozone* was prepared in the usual manner and was crystallised from ethanol as colorless plates, m. p. 162-63°. (Found : N, 13.3. $C_{19}H_{21}ON_3$ requires N, 13.67%).

2-[β-Methyl-β-(phenyl)-ethyl]-1-indanol (IVa).—A solution of the preceding compound (7 g.) in anhydrous ether (25 c.c.) was added to a well-stirred slurry of $LiAlH_4$ (0.54 g.) in anhydrous ether (30 c.c.) at a rate so as to maintain ether at gentle reflux. The resulting mixture was stirred and refluxed for additional 2 hours. After cooling, the contents were treated with iced HCl (50 c.c.) and the organic material was taken up in ether. The removal of the solvent followed by vacuum distillation furnished 6.3 g. (90%) of a colorless oil, b. p. 190-95°/10 mm. (Found : C, 85.45; H, 7.78. $C_{18}H_{20}O$ requires C, 85.67 ; H, 7.99 %).

* Melting and boiling points are uncorrected. Analyses by Drs. Weiler and Strauss, Oxford.

2-Methyl-1:2:10:11-tetrahydro-3:4-benzfluorene (Va).—Cold H_2SO_4 (*d* 1.84, 5 c. c.) was introduced dropwise to the above carbinol (5 g.), chilled to 0°, and the contents thoroughly mixed and left for 3 hours at 0°. The reaction mixture was then decomposed with powdered ice (10 g.) and worked up in the customary way, yielding 3 g. (65%) of a colorless viscous oil, b. p. 160-65°/10 mm. (Found : C, 92.10 ; H, 7.92. $C_{18}H_{18}$ requires C, 92.26 ; H, 7.74 %).

2-Methyl-3:4-benzfluorene (VIIa).—Dehydrogenation of the above compound (Va : 2 g.) was accomplished by heating with Pd--C (30%, 0.2 g.) at 300°-320° for 4 hours. The organic material was dissolved out in ether and the solvent was flashed off. The residual tan-yellow oily hydrocarbon, after regeneration from its picrate, crystallised from ethanol as cream-coloured flakes, m.p. 95-96°. (Found : C, 93.45 ; H, 5.9. $C_{18}H_{14}$ requires C. 93.87 ; H, 6.13 %).

The *picrate*, prepared in the usual way, was deposited as deep red needles which after two crystallisations from alcohol melted at 109-10°. (Found : N, 8.79. $C_{24}H_{17}O_7N_3$ requires N, 9.15%).

2-[β-Methyl β-(p-tolyl)-ethyl]-1-indanone (IIIb).—To well-stirred anhydrous thiophene-free toluene (100 c.c.) were introduced in lots and alternately anhydrous aluminium chloride (16 g.) and 2-allyl-1-indanone (II : 10 g.) during a total period of 80 minutes. After the addition was complete, the contents were stirred at 0°-5° for a further period of 5 hours and then worked up as in the case of (IIIa), yielding 14 g. (90%) of a viscous tan mass, b. p. 238-42°/10 mm, η_D^{19} 1.5841. (Found : C, 86.46 ; H, 7.83. $C_{19}H_{20}O$ requires C, 86.32 ; H, 7.63 %).

The 2 : 4-*dinitrophenylhydrazone* of (IIIb) after repeated crystallisations from ethyl acetate was obtained as orange-red needles, m. p. 80°. (Found : N, 12.4. $C_{25}H_{24}O_4N_4$ requires N, 12.61 %).

Oxidation of Ketone (IIIb) *with Alkaline Permanganate*.—The above ketone (IIIb : 2 g.) was refluxed with alkaline $KMnO_4$ solution (12.5 g. in 250 c.c. of water and 1-2 pellets of KOH) for about 12 hours when the colour of the permanganate discharged. Manganese dioxide was filtered off and the filtrate was concentrated to a small bulk and then acidified to precipitate out a mixture of phthalic acid and terephthalic acid. Terephthalic acid was converted into its dimethyl ester which after crystallisation melted at 142° (lit. m. p. 141-42°) which remained undepressed on admixture with an authentic sample.

2-[β-Methyl-β-(p-tolyl)-ethyl]-1 indanol (IVb).—A solution of (IIIb : 7 g.) in anhydrous ether (25 c. c.) was reduced with a suspension of $LiAlH_4$ (0.54 g.) in anhydrous ether (35 c.c.) in the manner of (IIIa). The usual working up of the reaction mixture afforded 6.2 g. (88%) of a viscous oil distilling at 220°/15 mm. (Found : C, 85.8 ; H, 8.10. $C_{19}H_{22}O$ requires C, 85.67 ; H, 8.33 %).

2 : 4'-Dimethyl-1 : 2 : 10 : 11-tetrahydro-3 : 4-benzfluorene (Vb).—Cyclisation of the above carbinol (IVb : 5 g.) was accomplished by treatment with H_2SO_4 (*d* 1.84, 5 c. c.) at 0° for 3 hours. The resulting cherry-brown mixture was worked up in the customary manner. Distillation of the product under vacuum afforded 3 g. (65%) of the hydro derivative (Vb) as a colorless viscous oil, b.p. 195°/15 mm. (Found : C, 91.9 ; H, 8.02. $C_{19}H_{20}$ requires C, 91.88 ; H, 8.12 %).

2 : 4′-*Dimethyl*-3 : 4-*benzfluorene* (VIIb).—The above hydro derivative (Vb : 2 g.) was treated with 30% Pd—C (0.2 g.) at 300°-320° for 4 hours. The aromatised product was subsequently extracted with dry ether and the solvent removed. The residual hydrocarbon was converted into its picrate and was regenerated therefrom as a solid mass which crystallised from ethanol as colorless leaflets, m.p. 64-65°. (Found : C, 93.60; H, 6.42. $C_{19}H_{16}$ requires C, 93.40 ; H, 6.60%).

The dark red *picrate* on two crystallisations from ethanol yielded needles, m. p. 96-97°. (Found : N, 9.15. $C_{25}H_{19}O_7N_3$ requires N, 9.20%).

The authors are indebted to Prof. S. M. Mukherji, Head of the University Chemistry Department, for his interest and valuable suggestions during the course of the present investigations.

Department of Chemistry,
Panjab University,
Hoshiarpur.

Received December 6, 1956

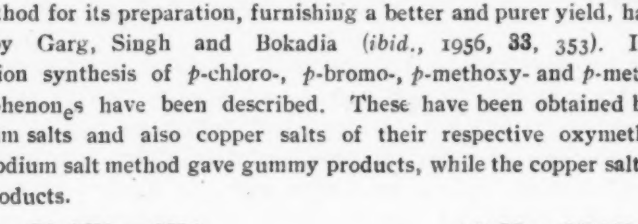
[Jour. Indian Chem. Soc , Vol. 34, No. 4, 1957]

SYNTHESIS OF *p*-SUBSTITUTED α-BROMO-α-FORMYLACETOPHENONES

By H. G. Garg and M. M. Bokadia

Synthesis and characterisation of bromo-oxymethylene-*p*-(chloro, bromo, methoxy and methyl)-acetophenones have been described. They have been obtained both from sodium and copper salts of their respective oxymethylene-ketones. The copper complex method has afforded, in general, better yields of purer products.

Bromo-oxymethylene-acetophenone (α-formyl-α-bromoacetophenone; (I, X=H) was prepared by Agarwal, Gupta and Deshapande (this *Journal*, 1949, **26**, 55) by the bromination of sodium salt of oxymethylene-acetophenone in dry carbon tetrachloride. Another method for its preparation, furnishing a better and purer yield, has been recently described by Garg, Singh and Bokadia (*ibid.*, 1956, **33**, 353). In the present communication synthesis of *p*-chloro-, *p*-bromo-, *p*-methoxy- and *p*-methyl-α-formyl-α-bromoacetophenones have been described. These have been obtained by the bromination of sodium salts and also copper salts of their respective oxymethylene-ketones. Generally, sodium salt method gave gummy products, while the copper salt method afforded purer products.



(I) (I)

[X=Br, Cl, OMe or Me]

The compounds were needed in connection with a synthetic work on heterocyclic compounds progressing in these laboratories.

The *p*-substituted bromo-oxymethylene-acetophenones are all colorless, crystalline compounds and respond to ferric chloride colour reaction ; they form copper chelate compounds and liberate iodine with acidified potassium iodide solution (cf. Bokadia and Deshapande, *ibid.*, 1950, **27**, 548 ; Bokadia, *Agra Univ. J. Res.*, 1953, II Sc., 9).

Copper complex of oxymethylene-*p*-aminoacetophenone has been synthesised and analysed. On bromination the copper complex gave a gummy product which could not be purified.

Experimental

p-Chloro-α-formyl-α-bromoacetophenone.—A mixture of *p*-chloroacetophenone (Vogel, "Organic Chemistry", Longmans Green and Co., London, 1948, p 696) (7.8 g.) and ethyl formate (5 c.c.) was gradually added in small instalments with constant shaking to a well-cooled suspension of sodium dust (1.4 g.) in dry ether. The contents were kept

at room temperature for two days with occasional shaking to complete the reaction. The sodium salt was filtered at the pump, washed with dry ether and dried. The sodium salt was suspended in CCl_4 and bromine (8 g.), dissolved in the same solvent, was added gradually to the suspension kept at ice temperature. The sodium bromide was filtered off and from the filtrate the solvent was removed on a water-bath. A thick syrup was left which gave a gummy mass (6.5 g.), pale yellow in colour, m.p. 90°. Crystallisation from dry benzene furnished a colorless product, m.p. 108°. (Found: C, 42.2; H, 2.71; Cl + Br, 43.2. $C_9H_6O_2ClBr$ requires C, 41 3; H, 2.3; Cl + Br, 44.1%).

In the other experiment the purified sodium salt was added to an excess of a saturated solution of copper acetate and the mixture was well shaken. The copper chelate compound was filtered, washed well with water and dried. The crude copper salt (m.p. 224°, 5 g.) was treated with bromine (4.9 g.) in the same manner as the sodium salt. The filtrate afforded a crystalline product (3.5 g., m.p. 102°) on evaporation and the pure product obtained on crystallisation, melted at 108°.

The bromo compound is insoluble in water but dissolves in dry benzene and absolute alcohol. It gives a violet colour with EtOH-$FeCl_3$. It forms copper chelate compound with copper acetate solution, melting above 275°, after purification. (Found: Cu, 10.24. $C_{18}H_{10}O_4Cl_2Br_2Cu$ requires Cu, 10. 86%).

On warming with acidified potassium iodide solution 1 g. mol. of the compound liberated 0.99 mol. of iodine.

p-*Bromo-α-formyl-α-bromoacetophenone.*—*p*-Bromoacetophenone (9.1 g.), obtained in the same manner as in case of *p*-chloroacetophenone (Vogel, *loc. cit.*) was formylated in the usual manner. The sodium salt was treated with bromine (8 g.). The filtrate on evaporation afforded a pale yellow gummy substance, crystallising from dry benzene in colorless solid, m.p. 114°, yield 6.8 g. (Found: C, 36.1; H, 2.1; Br, 52.6. $C_9H_6O_2Br_2$ requires C, 35.3; H, 1.99; Br, 52.2%).

The greenish blue copper complex of hydroxymethylene-*p*-bromoacetophenone (m.p. 260°, 6.5 g.) was treated with bromine (4.2 g.). The filtrate gave (3.0 g.) a solid product (m.p. at 98°) which after crystallisation melted at 114°.

The bromo compound is insoluble in water but dissolves in dry benzene and absolute alcohol. It develops a violet colour with EtOH-$FeCl_3$. It formed copper chelate compound, m.p. 204°. (Found: Cu, 9.2. $C_{18}H_{10}O_4Br_4Cu$ requires Cu, 9.45%). On warming with acidified potassium iodide solution, 1 g. mol. of the compound liberated 0.99 mol. of iodine.

p-*Methoxy-α-formyl-α-bromoacetophenone.*—The sodium salt of oxymethylene-*p*-methoxyacetophenone (7.8 g.) was treated with bromine (8 g.). The filtrate after recovering the solvent gave a syrupy liquid which on extraction with benzene furnished a pale yellow solid, m.p.104°. On further crystallisation with benzene it melted at 109°, yield 3.5 g. (Found: C, 45.9; H, 3.95; Br, 31.8. $C_{10}H_9O_3Br$ requires C, 46.6; H, 3.5; Br, 31.1%).

The greenish blue copper chelate salt of oxymethylene-*p*-methoxyacetophenone melted at 199° after recrystallisation from chloroform. (Found: Cu, 14.2. $C_{20}H_{18}O_6Cu$ requires Cu, 15.2.). On bromination it gave a crystalline solid product, m.p. 109°, yield 1.6 g.

The bromo compound is insoluble in water but dissolves in dry benzene and absolute alcohol. It gives a violet colour with ferric chloride. It formed a pale green copper chelate which crystallised from chloroform, m.p. 168°. (Found : Cu, 10.9. $C_{20}H_{16}O_6Br_2Cu$ requires Cu, 11.03%). On warming with acidified KI solution, 1 g. mol. of the compound liberated 0.98 mol. of iodine.

p-*Methyl-α-formyl-α-bromoacetophenone.*—*p*-Methylacetophenone (Vogel, *loc. cit.*) was formylated in the usual manner. The sodium salt (8 g.) was treated with bromine (8 g.) at ice temperature. The filtrate on evaporation gave a pale yellow solid (m.p. 103°) which after crystallisation from dry benzene melted at 106°. (Found : Br, 34.3. $C_{10}H_9O_2Br$ requires Br, 33.1%).

On warming with acidified KI solution 1 g. mol. of the compound liberated 0.98 mol. of iodine.

*Copper Chelate Compound of Oxymethylene-*p*-aminoacetophenone.*—The sodium salt of the oxymethylene compound (7 g.) was dissolved in water and treated with copper acetate solution when a greenish blue copper chelate salt separated, m.p. above 255° (decomp.), yield 6 g. (Found : Cu, 15.6. $C_{18}H_{16}O_4N_2Cu$ requires Cu, 16.38%).

The above copper complex (3 g.) was suspended in dry CCl_4 and to it bromine (1 mol.), dissolved in the same solvent, was added gradually. The filtrate on evaporation gave a gummy mass which could not be identified.

The authors' thanks are due to Dr. O. N. Perti, Professor and Head of the Chemistry Department, for his interest in the work.

CHEMICAL LABORATORIES,
TH. D. S B. GOVERNMENT COLLEGE,
NAINI TAL

Received July 11, 1956.

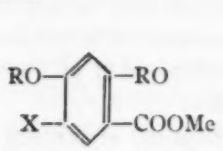
[Jour. Indian Chem. Soc., Vol. 34, No. 4, 1957]

FRIES AND FRIEDEL-CRAFTS' REACTIONS WITH METHYL 2:4-DIHYDROXY-5-SUBSTITUTED BENZOATES AND SYNTHESIS OF 4-SUBSTITUTED 2-ACYLRESORCINOLS

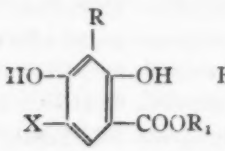
By J. I. Setalvad and N. M. Shah

Several 2-propionyl- and 2-butyryl-4-substituted resorcinols have been synthesised and condensed with ethyl acetoacetate.

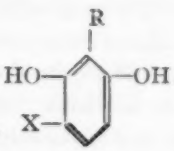
In continuation of our work (this *Journal*, 1952, **29**, 351, 915 ; 1953, **30**, 373 ; 1954, **31**, 600 ; 1955, **32**, 529) on the Fries migration of the esters of 5-substituted β-resorcylic acids and their methyl esters and subsequent synthesis of 4-substituted 2-acylresorcinols, several 2-propionyl- and 2-butyryl-4-substituted resorcinols are described in this communication.



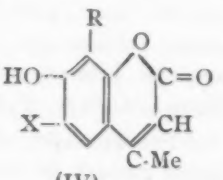
(I)



(II)



(III)



(IV)

Methyl 5-ethyl-, 5-bromo-, 5 chloro-2 : 4-dipropionoxybenzoates (I : R = -COEt ; X = Et, Br or Cl) afforded on migration below 130°, methyl 2 : 4-dihydroxy-3-propionyl-5-substituted benzoates and the corresponding acids (II : R = -COEt ; R_1 = Me and H ; X = Et, Br or Cl), hydrolysis occurring during the migration. The migration at higher temperature favours the hydrolysis of the keto-ester formed. The keto-esters (II : R = -COEt ; R_1 = Me) on alkaline hydrolysis furnished the keto-acids, identical with the same, obtained as migration products. The keto-acids on decarboxylation afforded 4-ethyl-, 4-bromo-, and 4-chloro-2-propionyl-resorcinols (III : R = -COEt ; X = Et, Br or Cl). For comparison, these were synthesised by starting from 6-ethyl-, 6-bromo- and 6-chloro-7-methylcoumarins by Limaye's Nidhone process (*Ber.*, 1932, **65**, 375 ; 1933, **67**, 12 ; *Rasayanam*, 1937, 80 ; 1939, 191 et seq), and were found identical.

The Friedel-Crafts propionylation of 5-substituted methyl β-resorcylates and the corresponding acids yielded the ketonic products, identical with the migration products.

The Friedel-Crafts butyrylation of methyl 2 : 4-dihydroxy-5-substituted benzoates or the corresponding acids afforded the keto-esters and/or acids [II : R = -COPr^n ; X = Et, Br or Cl ; R_1 = Me and/or H], 4-ethyl-, 4-bromo- and 4-chloro-2-butyrylresorcinols being obtained from the keto-acids by decarboxylation. The same keto-acids were also obtained independently by the Fries migration of the propionyl and butyryl derivatives of 5-bromo- and 5-chloro-β-resorcylic acids.

4-Substituted 2-acylresorcinols smoothly underwent the Pechmann condensation with ethyl acetoacetate giving rise to the keto-coumarins [IV : R = -COEt or -COPr^n ;

X=Et, Br or Cl], identical with the Fries migration products of the corresponding 7-acyloxy-6- substituted 4-methylcoumarins, thus establishing the structures of all the ketonic products described before.

EXPERIMENTAL

Methyl 2:4-Dipropionoxy-5-ethylbenzoate (I: R=COEt ; X=Et)

The compound (I: X=Et) was prepared by heating methyl 2:4-dihydroxy-5-ethylbenzoate (4 g.), propionic anhydride (6 c.c.) and H_2SO_4 (conc., drop) on a water-bath for 2 hours. The product, isolated as usual, crystallised from dilute alcohol in colorless plates, m.p. 89° (3 g.). (Found: C, 62.0 ; H, 6.4. $C_{16}H_{20}O_6$ requires C, 62.3 ; H, 6.5%). It is insoluble in alkali and does not respond to EtOH-$FeCl_3$ colour test.

Fries Migration of (I: R=-COEt ; X=Et).—The propionoxy-ester (3 g., 1 *M*) and anhydrous aluminium chloride were intimately mixed and heated at 110-20° for an hour ($CaCl_2$ guard-tube). The cold reaction mixture was then decomposed with crushed ice and HCl (conc., 5 c.c.). The solid obtained was filtered and treated with sodium bicarbonate solution (5%), when a part of it dissolved with effervescence. The bicarbonate-insoluble keto-ester crystallised from alcohol in yellow needles, m.p. 91° (0.8 g.). (Found: C, 61.6 ; H, 6.3. $C_{13}H_{16}O_5$ requires C, 61.9; H, 6.4%).

The keto-acid, obtained on acidifying the bicarbonate solution, crystallised from dilute ethanol in colorless needles, m.p. 183° (efferv.) (0.6 g.). (Found: C, 60.4 ; H, 5.7. $C_{12}H_{14}O_5$ requires C, 60.5 ; H, 5.9%).

The *dibenzoyl* derivative of the keto ester, prepared by benzoyl chloride-pyridine method, crystallised from alcohol in colorless needles, m.p. 114°. (Found: C, 70.2 ; H, 5.1. $C_{27}H_{24}O_7$ requires C, 70.4 ; H, 5.2%).

Friedel-Crafts' Propionylation of (I: R=H ; X=Et).—Methyl 2:4-dihydroxy-5-ethylbenzoate (2.5 g.) and propionic anhydride (2.5 c.c.) were added to a cold solution of aluminium chloride (3.5 g.) in dry nitrobenzene (30 c.c.) with shaking and cooling. The mixture was left at 25-30° for 20 hours and then heated at 105° for 4 hours ($CaCl_2$ guard-tube). On decomposition with ice and HCl (conc., 5 c.c.) and removal of nitrobenzene by steam-distillation, the solid obtained was treated with 5% NaOH solution; the yellow alkaline filtrate on acidification furnished a solid having no sharp m.p. It was therefore treated with bicarbonate solution (5%) and the keto ester and acid were separated and crystallised as before. Their mixed melting points with the migration products obtained before remained undepressed.

Hydrolysis of (II: R=-COEt; X=Et ; R_1=Me) (0.8 g.) by 10% NaOH solution (20 c.c.) at room temperature for 24 hours afforded on acidification 2:4-dihydroxy-3-propionyl-5-ethylbenzoic acid which crystallised from dilute ethanol, m.p. 183° (efferv.), identical with the same acid obtained before.

Formation of 4-Ethyl-2-propionylresorcinol (III: R=-COEt ; X=Et).—The keto-acid (1 g.) in water (80 c.c.), acetic acid (1 c.c.) and a few drops of HCl (conc.) were refluxed on a sand-bath for 20 hours and then filtered hot. The filtrate on cooling and diluting afforded a yellow solid, which crystallised from water in needles, m.p. 102° (0.3 g.),

undepressed with the hydrolysis product of 8-propionyl-7-hydroxy-6-ethyl-4-methylcoumarin (*vide infra*). (Found: C, 67.9; H, 7.2. $C_{11}H_{14}O_3$ requires C, 68.0; H, 7.2%). It developed a green colour with EtOH-$FeCl_3$ and a yellow colour with alkali. It is easily soluble in alcohol and in other common organic solvents.

8-Propionyl-7-hydroxy-6-ethyl-4-methylcoumarin (IV: R = -COEt; X = Et).—4-Ethyl-2-propionylresorcinol (0.5 g.) was mixed with ethyl acetoacetate (1.0 g.) in presence of H_2SO_4 (80%, 3 c.c.) in cold and then left overnight at room temperature. On treating with ice-cold water, a yellow solid was obtained which crystallised from alcohol in lustrous yellow needles, m.p. 111°, undepressed with the Fries migration product of 7-propionoxy-6-ethyl-4-methylcoumarin.

7-Propionoxy-6-ethyl-4-methylcoumarin was prepared by heating 7-hydroxy-6-ethyl-4-methylcoumarin (5 g.) with propionic anhydride (6 c.c.) in presence of H_2SO_4 (conc., drop) for 2 hours. On working it up as usual, it crystallised from ethanol in colorless needles, m.p. 154° (4 g.). (Found: C, 69.0; H, 6.0. $C_{13}H_{14}O_4$ requires C, 69.2; H, 6.2%). It did not develop any colour with alcoholic ferric chloride.

Fries Migration.—An intimate mixture of the above propionoxy-coumarin (3 g., 1 *M*) and anhydrous aluminium chloride (5 g., 3.3 *M*) was baked at 140-50° for an hour ($CaCl_2$ guard-tube); fumes of HCl gas evolved vigorously at 125°. On working up as before, the product obtained was crystallised from ethanol in yellow shining needles, m.p. 111° (1.2 g.). (Found: C, 69.1; H, 6.1. $C_{13}H_{14}O_4$ requires C, 69.2; H, 6.2%). It dissolved in alkali with non-fluorescent yellow colour and developed a brown colour with EtOH-$FeCl_3$.

The *acetoxy* derivative, prepared by acetic anhydride-pyridine method, crystallised from ethanol in colorless lustrous needles, m.p. 137°. (Found: C, 67.4; H, 6.0. $C_{17}H_{18}O_5$ requires C, 67.5; H, 6.0%).

The *benzoyloxy* derivative, prepared by benzoyl chloride-pyridine method, crystallised from dilute ethanol in colorless needles, m.p. 130°. (Found: C, 72.3; H, 5.4. $C_{22}H_{20}O_5$ requires C, 72.5; H, 5.5%). The *semicarbazone*, prepared by usual method, crystallised from alcohol in fibrous needles, m.p. 208° (decomp.). [Found: N, 13.0. $C_{16}H_{19}O_4N_3$ requires N, 13.2%].

Hydrolysis of the Keto-coumarin (IV: R = -COEt; X = Et).—The keto-coumarin (1 g.) in 10% NaOH (25 c.c.) was refluxed on a sand-bath for 2 hours and then filtered hot. On acidifying the cold filtrate, a puffy solid was obtained. It crystallised from water in yellow needles, m.p. 102°, undepressed with the sample obtained before.

Friedel-Crafts' Butyrylation of Methyl 2:4-dihydroxy-5-ethylbenzoate.—Methyl 2:4-dihydroxy-5-ethylbenzoate (3 g.) was added in small instalments to a cold solution of aluminium chloride (4.2 g.) in dry nitrobenzene (40 c.c.). *n*-Butyric anhydride (3 c.c.) was then added slowly with cooling. The mixture was left overnight at room temperature and then heated at 100-105° for 4 hours ($CaCl_2$ guard-tube). It was then cooled and worked up as before. The solid obtained after steam-distillation of nitrobenzene was treated with bicarbonate solution as before. The keto-ester crystallised from ethanol in straw-coloured needles, m.p. 66° (0.8 g.). (Found: C, 63.1; H, 6.6. $C_{14}H_{18}O_5$ requires C, 63.2; H, 6.8%). The keto-acid crystallised from dilute ethanol in fibrous

needles, m.p. 181° (efferv.) (0.6 g.) (Found: C, 61.8; H, 6.3. $C_{13}H_{16}O_5$ requires C, 61.9; H, 6.4%). The keto-ester developed a purple colour and the acid, a violet colour with EtOH-$FeCl_3$. Both exhibited a yellow colour with alkali.

The *dibenzoyl* derivative of the keto-ester crystallised from alcohol in colorless needles, m.p. 108°. (Found: C, 70.7; H, 5.4. $C_{28}H_{26}O_7$ requires C, 70.9; H, 5.5%).

Hydrolysis: Formation of 2:4-Dihydroxy-3-butyryl-5-ethylbenzoic Acid.—The ester (0.6 g.) in 10% NaOH (20 c.c.) was heated on a water-bath for an hour and then kept overnight at room temperature. The solid obtained on acidification was treated with bicarbonate solution (5%). The filtrate, on acidification afforded a solid, which crystallised from dilute ethanol, m.p. 181° (efferv.), mixed melting point with the keto-acid obtained before remaining undepressed.

Decarboxylation of the keto-acid (II: R = -$COPr^n$; X = Et; R_1 = H) (0.8 g.) with acidulated water as before gave 4-ethyl-2-butyrylresorcinol (III: R = -$COPr^n$; X = Et). It crystallised from water in yellow needles, m.p. 80° (yield 25%), identical with the hydrolysis product of 8-butyryl-7-hydroxy-6-ethyl-4-methylcoumarin. (Found: C, 69.1; H, 7.5. $C_{12}H_{16}O_3$ requires C, 69.2; H, 7.7%). It showed a green colour with EtOH-$FeCl_3$.

The *Pechmann condensation of* (III: R = -$COPr^n$; X = Et) (0.5 g.) with ethyl acetoacetate (1 g.) in presence of H_2SO_4 (80%, 3 c.c.) as before, afforded 8-butyryl-7-hydroxy-6-ethyl-4-methylcoumarin, which crystallised from ethanol in yellow needles, m.p. 110°, identical with the coumarin obtained by the Fries migration of 7-butyroxy 6-ethyl-4-methylcoumarin.

7-Butyroxy-6-ethyl-4 methylcoumarin, prepared by heating the hydroxy-coumarin (5 g.), *n*-butyric anhydride (6 c.c.) and H_2SO_4 (conc., drop) as before, crystallised from ethanol in shining needles, m.p. 125° (4 g.). (Found: C, 70.0; H, 6.5. $C_{18}H_{18}O_4$ requires C, 70.1; H, 6.6%).

Fries Migration.—The butyroxy-coumarin (3 g., 1 *M*) and aluminium chloride (5.5 g., 3.3 *M*) were heated at 140-50°. On working up as before, the product crystallised from ethanol in yellow needles, m.p. 110° (1.2 g.). (Found: C, 70.2; H, 6.4. $C_{16}H_{16}O_4$ requires C, 70.1; H, 6.6%). It showed a reddish brown colour with EtOH-$FeCl_3$. The *acetoxy* derivative of the keto-coumarin crystallised from methanol in colorless needles, m.p. 114°. (Found: C, 68.1; H, 6.2. $C_{18}H_{20}O_5$ requires C, 68.4; H, 6.3%).

The *oxime* crystallised from alcohol in colorless needles, m.p. 167° (decomp.). (Found: N, 4.6. $C_{16}H_{19}O_4N$ requires N, 4.8%).

Formation of 4-Ethyl-2-butyrylresorcinol (III: R = -$COPr^n$; X = Et).—The keto-coumarin (0.8 g.) on alkaline hydrolysis as before afforded a product which crystallised from hot water in yellow needles, m.p. 80° (0.2 g.), mixed melting point with the sample obtained before being undepressed.

Methyl 2:4-Dipropionoxy-5-bromobenzoate (I: R = -COEt; X = Br)

The compound (I: X = Br) was obtained by heating methyl 5-bromo-β-resorcylate (5 g.), propionic anhydride (7 c.c.) and H_2SO_4 (conc., drop) as before. It crystallised from acetic acid in colorless plates, m.p. 122° (3.5 g.). (Found: Br, 22.0. $C_{14}H_{15}O_6Br$ requires Br, 22.3%).

Fries Migration of (I : R = -COEt ; X=Br).—(*i*). The propionoxy-ester (3 g., 1 *M*) and $AlCl_3$ (4.5 g., 3.3 *M*) were heated at 125-30° for an hour, HCl gas evolving at 100°. On working it up as before, the product obtained was found to be a mixture. It was treated with sodium bicarbonate solution (5%), when it partly dissolved with effervescence. The bicarbonate-insoluble portion crystallised from alcohol in yellow silky needles, m.p. 120° (0.8 g.). (Found : Br, 26.2. $C_{11}H_{11}O_5Br$ requires Br, 26.4%).

The bicarbonate solution on acidification provided a pale yellow puffy solid, which crystallised from dilute alcohol in needles, m.p. 219-20° (efferv.) (0.6 g.). (Found : Br, 27.4. $C_{10}H_9O_5Br$ requires Br, 27.7%). The keto-ester developed a red colour and the acid, a purple colour with alcoholic ferric chloride.

(*ii*). The above migration at 160-70° gave only the keto-acid, identified by its mixed m.p. with an authentic sample.

(*iii*). The above migration, when carried out using nitrobenzene (40 c.c.) as a solvent at room temperature for 24 hours or at 100° for an hour, also gave the same keto-ester and acid, identified by their mixed m. p. with authentic samples.

Methyl 5-bromo-β-resorcylate was propionated by propionic anhydride under the conditions of the Friedel-Crafts reaction as before. The keto-ester and the acid obtained were found identical with the migration products.

The *dibenzoyl* derivative of the keto-ester crystallised from alcohol in colorless needles, m.p. 129°. (Found : Br, 15.4. $C_{25}H_{19}O_7Br$ requires Br, 15.7 %).

The *semicarbazone* crystallised from dilute alcohol in colorless fibrous needles, m.p. 196° (decomp.). (Found : N, 11.4. $C_{12}H_{14}O_5N_3Br$ requires N, 11.7 %).

Hydrolysis of the keto-ester (II : R = -COEt ; X = Br ; R_1 = Me) (1 g.) was carried out as before. The acid (II : R = -COEt ; X = Br ; R_1 = H) obtained was crystallised from dilute alcohol in needles, m.p. 219° (efferv.), undepressed with the same obtained by the Fries migration.

2-Hydroxy-4-propionoxy-5-bromobenzoic acid, prepared by heating 5-bromo β-resorcylic acid (5 g.) with propionic anhydride (6.5 c.c.) and pyridine (2 drops) at 100° for 4 hours as before, crystallised from dilute alcohol in buff-coloured needles, m.p. 166° (2.5 g.). (Found : Br, 27.5. $C_{10}H_9O_5Br$ requires Br, 27.7 %). It developed a violet colour with EtOH-$FeCl_3$.

Fries Migration.—The above propionoxy-acid (3 g., 1 *M*) and $AlCl_3$ (4.8 g., 3.3 *M*) were heated together at 165-70° for an hour and worked up as before. The keto-acid obtained was purified by bicarbonate solution (5%) treatment. It crystallised from dilute alcohol in needles, m.p. 219° (efferv.) (1 g.) ; mixed m.p. with the same acid obtained above remained undepressed.

The migration at a higher temperature gave poor yields of the keto-acid.

Friedel-Crafts' propionylation of 5-bromo-β-resorcylic acid was carried out as before. 2 : 4-Dihydroxy-3-propionyl-5-bromobenzoic acid was obtained, m. p. 219° (efferv.).

The *methyl ester*, prepared by esterifying it is before, was identical with the migration product.

Formation of 4-Bromo-2-propionylresorcinol (III: R = -COEt ; X = Br).—The keto-acid (0.5 g.) was decarboxylated as before. The product crystallised from hot water as yellow needles, m.p. 115° (0.15 g.). (Found: Br, 32.4. $C_9H_9O_3Br$ requires Br, 32.7%). It showed a green colour with EtOH-$FeCl_3$.

8-Propionyl-7-hydroxy-6-bromo-4-methylcoumarin (IV: R = -COEt ; X=Br) was obtained by the Pechmann condensation of 4-bromo-2-propionylresorcinol with ethyl acetoacetate as before. It crystallised from acetic acid in lustrous needles, m. p. 198°, undepressed with the keto-coumarin obtained by the Fries migration of 7-propionoxy-6-bromo-4-methylcoumarin.

7-Propionoxy-6-bromo-4-methylcoumarin crystallised from alcohol in colorless lustrous needles, m.p. 128° (3 g.). (Found: Br, 25.3. $C_{13}H_{11}O_4Br$ requires Br, 25.7%).

Fries Migration.—The above propionoxy-coumarin (3 g., 1*M*) and $AlCl_3$ (anhyd., 5 g., 3.3 *M*) were heated at 150° for an hour. On working up as before, the product crystallised from acetic acid in yellow needles, m.p. 198° (1.2 g.), identical with the keto-coumarin obtained by the Pechmann condensation. (Found: Br, 26.0. $C_{13}H_{11}O_4Br$ requires Br, 25.7%). It developed a reddish brown colour with EtOH-$FeCl_3$ and dissolved in alkali with a non-fluorescent yellow colour.

The *acetoxy* derivative crystallised from ethanol in colorless needles, m.p. 166°. (Found: Br, 22.4. $C_{15}H_{13}O_5Br$ requires Br, 22.7%).

The *benzoyloxy* derivative crystallised from ethanol in needles, m. p. 159°. (Found: Br, 19.4. $C_{20}H_{15}O_5Br$ requires Br, 19.3%).

The *oxime* crystallised from dilute ethanol in colorless granules, m. p. 216° (decomp.). (Found: N, 4.0. $C_{13}H_{12}O_4NBr$ requires N, 4.3 %).

Friedel-Crafts' Butyrylation of Methyl 2:4-Dihydroxy-5-bromobenzoate.—The bromo-ester (3 g.) and *n*-butyric anhydride (2.5 c.c.) were added to the solution of $AlCl_3$ (4 g.) in nitrobenzene (30 c. c.) and heated as before. On working up as usual the keto-ester crystallised from alcohol in yellow needles, m.p. 107° (0.8 g.). (Found: Br, 25.4. $C_{13}H_{15}O_5Br$ requires Br, 25.2%). The keto-acid crystallised from dilute alcohol in needles, m.p. 211° (efferv.). (Found: Br, 26.3. $C_{11}H_{11}O_5Br$ requires Br, 26.4%).

Both the keto-ester and the acid showed colour reaction with EtOH-$FeCl_3$.

Friedel-Crafts' butyrylation of 5-bromo-β-resorcylic acid as above gave the same keto-acid (II: R = -$COPr^n$; X = Br ; R_1=H).

The keto-ester (II: R = -$COPr^n$; X = Br ; R = Me) on hydrolysis as before furnished the keto-acid, identical with one obtained above.

The *oxime* of the keto-ester crystallised from dilute alcohol in colorless granules, m.p. 166° (decomp.). (Found: N, 4.0. $C_{13}H_{14}O_5NBr$ requires N, 4.2%).

Fries Migration of 2-Hydroxy-4-O-butyryl-5-bromobenzoic Acid.—*2-Hydroxy-4-butyroxy-5-bromobenzoic acid*, prepared by heating 5-bromo-β-resorcylic acid with *n*-butyric anhydride and pyridine as before, crystallised from dilute alcohol in colorless needles, m.p. 146°. (Found: Br, 26.2. $C_{11}H_{11}O_5Br$ requires Br, 26.4%).

The above butyroxy-acid (3 g.) was heated with $AlCl_3$ (5 g.) at 170-75° for an hour and then worked up as before. The keto-acid obtained crystallised from dilute alcohol in needles, m.p. 211° (efferv.).

The keto-acid (II: R = -COPr^n; X = Br; R_1 = H) on decarboxylation as before, afforded a product which crystallised from water in yellow fibrous needles, m.p. 108-109°, identified as 4-bromo-2-butyrylresorcinol (III: R = -COPr^n; X = Br). (Found: Br, 30.6. $C_{10}H_{11}O_3Br$ requires Br, 30.9%). It showed a green colour with EtOH-$FeCl_3$. It condensed with ethyl acetoacetate in presence of H_2SO_4 (80%) as before, yielding 8-butyryl-7-hydroxy-6-bromo-4-methylcoumarin. It crystallised from alcohol in yellow needles, m.p. 157° (3 g.), identical with the migration product of 7-butyroxy 6-bromo-4-methylcoumarin.

8-Butyryl-7 hydroxy-6-bromo-4-methylcoumarin (IV: R = -COPr^n; X = Br).—*7-Butyroxy-6-bromo-4-methylcoumarin*, prepared as before, crystallised from alcohol in colorless shining plates, m.p. 120° (4 g.). (Found: Br, 24.2. $C_{14}H_{13}O_4Br$ requires Br, 24.6%).

The butyroxy-coumarin (3 g., 1 *M*) was heated with $AlCl_3$ (4.5 g., 3.3 *M*) at 145-50° for an hour and worked up as before. The solid obtained was crystallised from alcohol in glistening yellow needles, m.p. 156° (1.2 g.), identical with the keto-coumarin obtained before by the Pechmann condensation. (Found: Br, 24.2. $C_{14}H_{13}O_4Br$ requires Br, 24.6%). It developed a reddish brown colour with EtOH-$FeCl_3$ and dissolved in alkali with a non-fluorescent yellow colour.

The *acetoxy* derivative crystallised from alcohol in colorless needles, m.p. 128°. (Found: Br, 22.5. $C_{16}H_{15}O_5Br$ requires Br, 21.8%).

The *benzoyloxy* derivative crystallised from alcohol in colorless lustrous cubes, m.p. 151°. (Found: Br, 18.4. $C_{21}H_{17}O_5Br$ requires Br, 18.6%).

The *semicarbazone*, prepared as usual, crystallised from dilute alcohol in colorless granules, m.p. 231° (decomp.). (Found: N, 10.5. $C_{18}H_{16}O_4N_3Br$ requires N, 10.9%).

Methyl 2:4-Dipropionoxy-5-chlorobenzoate (I: R = -COEt; X = Cl)

For sake of brevity, the experimental details have been omitted in this part, as they are generally identical with the corresponding bromo compounds, already described.

The compound (I: R=-COEt; X=Cl) crystallised from alcohol in colorless lustrous needles, m.p. 114°. (Found: Cl, 11.0. $C_{14}H_{13}O_6Cl$ requires Cl, 11.3%).

Fries Migration of (I, R= -COEt; X=Cl).—A mixture of the propionoxy-ester (3 g.) and $AlCl_3$ (4.5 g.) was heated at 125-30° for an hour and worked up as before. The acid and ester were separated by bicarbonate treatment. The ester crystallised from acetic acid in yellow fleecy needles, m.p. 107° (0.9 g.). (Found: Cl, 13.6. $C_{11}H_{11}O_5Cl$ requires Cl, 13.7%). The keto-acid crystallised from dilute alcohol in pale yellow needles, m. p. 206° (efferv.) (0.5 g.). (Found: Cl, 14.3. $C_{10}H_9O_5Cl$ requires Cl, 14.5%).

Both the keto-ester and the acid showed colour reaction with alcoholic ferric chloride. The keto-ester on alkaline hydrolysis as before afforded the acid, identical with the keto-acid obtained above.

Friedel-Crafts' propionylation of methyl 2:4-dihydroxy-5-chlorobenzoate and the corresponding acid (3 g.) with propionic anhydride (2.5 c.c.) under similar conditions described for the bromo compounds yielded the keto-ester (II: R = -COEt; X=Cl; R_1=Me) and the corresponding keto-acid, identical with the migration products.

The *dibenzoate* of the keto-ester crystallised from alcohol in colorless lustrous plates, m.p. 124°. (Found : Cl, 7.3. $C_{25}H_{19}O_7Cl$ requires Cl, 7.6%).

The *semicarbazone* of the keto-ester crystallised from dilute alcohol in colorless needles, m.p. 198° (decomp.). (Found : N, 13.0. $C_{12}H_{14}O_5N_3Cl$ requires N, 13.3%).

Fries Migration of 2-Hydroxy-4-O-propionyl-5-chlorobenzoic Acid.—*2-Hydroxy-4-propionoxy-5-chlorobenzoic acid*, prepared as before, crystallised from dilute alcohol in silvery flakes, m.p. 155°. (Found : Cl, 14.4. $C_{10}H_9O_5Cl$ requires Cl, 14.5 %).

The above propionoxy-acid (2.5 g.) was mixed with $AlCl_3$ (5 g.) and heated at 165° for an hour. It was worked up as before. The solid obtained crystallised from dilute alcohol in needles, m.p. 207° (efferv.) (0.8 g.), undepressed with the sample obtained before.

The *methyl ester* of the above keto-acid, prepared by esterification, crystallised from acetic acid in yellow needles, m. p. 107°, identical with the migration product.

The *decarboxylation of the keto-acid* by acidulated water, as before, gave 4-chloro-2-propionylresorcinol, (III : R = -COEt ; X=Cl), crystallised from dilute alcohol in yellow needles, m.p. 107°, undepressed on admixture with the same, synthesised from 8-propionyl-7-hydroxy-6-chloro-4-methylcoumarin. (Found: Cl, 17.6. Calc. for $C_9H_9O_3Cl$: Cl, 17.7%). It showed a green colour with EtOH-$FeCl_3$ and dissolved in alkali with a yellow colour.

The *Pechmann condensation* of (III : R = -COEt ; X=Cl) (0.5 g.) with ethyl aceto-acetate (1.5 g.) in presence of H_2SO_4 (80%, 4 c.c.) as before gave the keto-coumarin (IV : R = -COEt ; X=Cl). It crystallised from alcohol in yellow needles, m. p. 181° (0.4 g.), undepressed with the migration product of 7-propionoxy-6-chloro 4-methyl-coumarin.

7-Propionoxy-6-chloro-4-methylcoumarin, prepared as before, was crystallised from ethanol in colorless needles, m. p. 111°. (Found : Cl, 13.1. $C_{13}H_{11}O_4Cl$ requires Cl, 13.3 %).

Fries Migration.—The propionoxy-coumarin (3 g.) and $AlCl_3$ (5 g.) were heated at 140-50° for an hour and worked up as before. The product crystallised from a mixture of alcohol and a few drops of acetic acid in yellow needles, m. p. 181° (1.2 g.), undepressed with the same keto-coumarin obtained before. (Found : Cl, 13.1. $C_{13}H_{11}O_4Cl$ requires Cl, 13.3%). It developed a reddish brown colour with alcoholic ferric chloride.

The *acetoxy* derivative of the keto-coumarin crystallised from dilute alcohol in colorless needles, m.p. 168°. (Found : Cl, 11.4. $C_{15}H_{13}O_5Cl$ requires Cl, 11.5%).

The *benzoyloxy* derivative crystallised from alcohol in clusters of colorless needles, m. p. 171°. (Found : Cl, 9.4. $C_{20}H_{15}O_5Cl$ requires Cl, 9.6%).

The *semicarbazone* crystallised from alcohol in pale yellow needles, m. p. 216° (decomp.). (Found : N, 12.6. $C_{14}H_{14}O_4N_3Cl$ requires Cl, 12.9%).

The keto-coumarin on hydrolysis as before gave 4-chloro-2-propionylresorcinol (III : R = -COEt ; X = Cl). It crystallised from dilute alcohol in yellow needles, m. p. 107°.

The *dibenzoyl* derivative of (III : R=- COEt ; X=Cl) crystallised from alcohol in colorless plates, m.p. 120°. (Found : Cl, 8.4. $C_{23}H_{17}O_5Cl$ requires Cl, 8.7%).

Friedel-Crafts' butyrylation of (I : R = H ; X = Cl) and the corresponding acid as before furnished the keto-ester (II : R = -COCPr^n ; X = Cl ; R_1 = Me) and the corresponding keto-acid. The keto-ester crystallised from acetic acid in yellow silky needles, m.p. 100°. (Found : Cl, 13.2. $C_{12}H_{13}O_5Cl$ requires Cl, 13.0%). The keto-acid crystallised from dilute alcohol in pale yellow needles, m. p. 202° (efferv.). (Found : Cl, 13.5. $C_{11}H_{11}O_5Cl$ requires Cl, 13.7%). They showed red colour with EtOH-$FeCl_3$.

The *dibenzoyl* derivative of the keto-ester crystallised from alcohol in colorless truncated needles, m.p. 101°. (Found : Cl, 7.1. $C_{26}H_{21}O_7Cl$ requires Cl, 7.4%).

The *oxime* of the keto-ester crystallised from dilute alcohol in shining needles, m.p. 167° (decomp.). (Found N, 4.7. $C_{12}H_{14}O_5NCl$ requires N, 4.9%).

The keto-ester on alkaline hydrolysis as before gave the keto-acid (II : R = -COPr^n ; X = Cl ; R_1 = H), identical with the migration product.

Fries Migration of 2-Hydroxy-4-O-butyryl-5-chlorobenzoic Acid.—*2-Hydroxy-4-butyroxy-5-chlorobenzoic acid* was crystallised from dilute alcohol in silvery flakes, m. p. 145°. (Found : Cl, 13.8. $C_{11}H_{11}O_5Cl$ requires Cl, 13.7%).

The above butyroxy-acid (3 g.) was heated with $AlCl_3$ (4.8 g.) at 145° for an hour and worked up as before. The product crystallised from dilute alcohol in pale yellow needles, m.p. 203° (efferv.), undepressed with the keto-acid obtained before.

The keto-acid was decarboxylated to 4-chloro-2-butyrylresorcinol (III : R = -COPr^n ; X = Cl) as before. It crystallised from dilute alcohol in yellow needles, m.p. 115°, undepressed with the hydrolysis product of 8-butyryl-7-hydroxy-6-chloro-4-methylcoumarin (IV : R = -COPr^n ; X = Cl). (Found : Cl, 16.2. $C_{10}H_{11}O_3Cl$ requires Cl, 16.6%). It showed a green colour with EtOH-$FeCl_3$.

4-Chloro-2-butyrylresorcinol condensed with ethyl acetoacetate as before, furnishing the keto-coumarin (IV : R = -COPr^n ; X = Cl), which crystallised from alcohol in yellow fibrous needles, m. p. 153°, identical with the same obtained by the Fries migration.

7-Butyroxy-6-chloro 4-methylcoumarin crystallised from alcohol in colorless lustrous plates, m.p. 119°. (Found : Cl, 12.4. $C_{14}H_{13}O_4Cl$ requires Cl, 12.7%).

The above butyroxy-coumarin (3 g.) was heated with $AlCl_3$ (4.8 g.) at 145-50° for one hour and worked up as before. The product crystallised from alcohol in yellow needles, m.p. 153° (1 g.), undepressed with the same keto-coumarin obtained before. (Found : Cl, 12.5. $C_{14}H_{13}O_4Cl$ requires Cl, 12.7%). It showed a red colour with EtOH-$FeCl_3$.

The *acetoxy* derivative crystallised from ethanol in colorless needles, m. p. 139°. (Found : Cl, 10.9. $C_{16}H_{15}O_5Cl$ requires Cl, 11.0%).

The *benzoyloxy* derivative crystallised from ethanol in colorless lustrous cubes, m.p. 144°. (Found : Cl, 9.1. $C_{21}H_{17}O_5Cl$ requires Cl, 9.2%).

The *oxime* crystallised from alcohol in colorless needles, m. p. 197° (decomp.). (Found: N, 4.4. $C_{14}H_{14}O_4NCl$ requires N, 4.7%).

The keto-coumarin (IV: R = -COPr^n; X=Cl) was hydrolysed with sodium hydroxide (12%) as before and 4-chloro-2-butyrylresorcinol (III: R = -COPr^n; X=Cl) was obtained. It crystallised from dilute alcohol in yellow needles, m.p. 115°.

The *dibenzoate* of (III: R = -COPr^n; X=Cl) crystallised from alcohol in colorless plates, m.p. 123°. (Found: Cl, 8.1. $C_{24}H_{19}O_5Cl$ requires Cl, 8.4%).

M. R. Science Institute,
Gujarat College, Ahmedabad-6
and
St. Xaviers College,
Ahmedabad-6.

Received July 3, 1956.

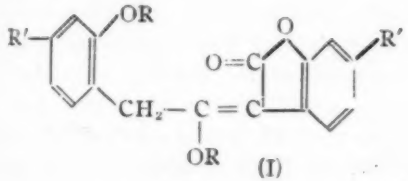
[Jour. Indian Chem. Soc., Vol. 34, No. 4, 1957]

EXPERIMENTS ON THE SYNTHESES OF FURANO COMPOUNDS. PART XII. FURTHER TRANSFORMATIONS OF *iso*COUMARANONE

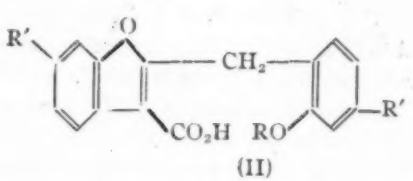
By J. N. Chatterjea

The self-condensation product of *iso*coumaranone has been converted into β-brazan. The constitutions of acid-catalysed transformation products of 3-acyl-*iso*coumaranones have been elucidated. The self-condensation of 6-methoxy*iso*coumaranone has also been studied.

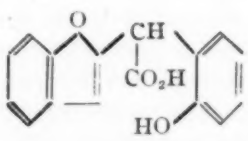
In Part VI of this series of papers (this *Journal*, 1956, **33**, 175), it has been shown that *iso*coumaranone undergoes self-condensation in presence of sodium hydride, yielding 3-*o*-hydroxyphenylacetylcoumaranone-2 which exists largely in the enolic form (I: R=R′=H). When this compound was boiled with hydrochloric acid in acetic acid, an isomeric phenolic acid was formed in excellent yield which was formulated as either (II : R=R′=H) or (III).



(I)



(II)

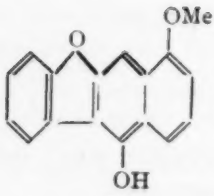


(III)

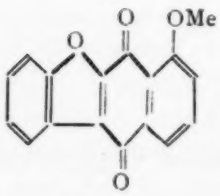
The ambiguity has now been cleared and the isomeric acid has been shown to have the structure (II : R=R′=H) on the following grounds :

(*i*) The dimethyl ether (I : R=Me ; R′=H) obtained by the action of diazomethane on the self-condensation product gave, on acid treatment, a methoxy-carboxylic acid, identical with the product obtained on methylation of the above mentioned isomeric phenolic acid. From this, it is clear that the phenolic hydroxy group of (I : R=R′=H) *did not* take part in this transformation, and thus excluding the structure (III) for the isomeric acid.

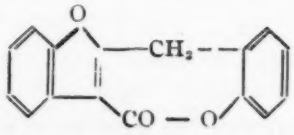
(*ii*) The acid chloride derived from the above mentioned methoxy-carboxylic acid gave, on treatment with aluminium chloride, a naphthol, recognised by typical colour reaction with chloroform and alkali (Perkin and Robinson, *J. Chem. Soc.*, 1909, **95**, 381).



(IV)



(V)

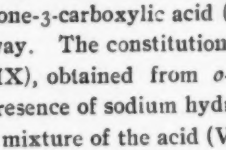


(VI)

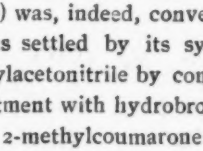
It is clear therefore that the acid and the naphthol have respectively the structures (II : R=Me; R′=H) and (IV). Further, this α-naphthol on oxidation with chromic acid furnished 7-methoxy-β-brazanquinone (V) which afforded a small quantity of β-brazan on vigorous treatment with hydriodic acid, and thus providing an example of unique formation of β-brazan from *iso*coumaranone†. In agreement, 7-methoxy-β-brazan also afforded a small amount of β-brazan on similar treatment.

The phenolic acid (II: R=R′=H) affords a lactone on treatment with propionic anhydride. This compound, now prepared with thionyl chloride, has undoubtedly the structure (VI). An attempt to prepare this lactone or (II: R=R′=H) by the Wolff-Kishner reduction of the related ketone (VI : CO in place of CH_2 ; this *Journal*, 1955, **32**, 265) resulted in the exclusive formation of the corresponding azine.

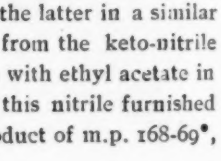
It may be noted that in the formation of the acid (II : R=R′=H) from (I : R=R′=H), the furan ring is broken down and then reconstituted. This interesting transformation is found to be general. Thus, the self-condensation product of 6-methoxy*iso*coumaranone was isomerised by hydrochloric acid in acetic acid to (II : R=H ; R′=OMe). Again, 3-acetylcoumaranone-2 (VII : R=Me) (or its acetyl derivative) which was originally regarded by Pfeiffer and Enders (*Chem. Ber.*, 1951, **84**, 247) as 2-methylcoumarone-3-carboxylic acid (VIII ; R=Me) was, indeed, converted into the latter in a similar way. The constitution of the acid was settled by its synthesis* from the keto-nitrile (IX), obtained from *o*-methoxyphenylacetonitrile by condensation with ethyl acetate in presence of sodium hydride. On treatment with hydrobromic acid, this nitrile furnished a mixture of the acid (VIII : R=Me), 2-methylcoumarone and a product of m.p. 168-69°, probably a polymeride of 2-methylcoumarone.



(VII)



(VIII)



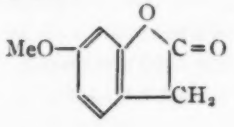
(IX)

In a like manner, 3-propionylcoumaranone-2 and 6-methoxy-3-acetylcoumaranone-2 were isomerised to 2-ethylcoumarone-3-carboxylic acid and 6-methoxy-2-methycoumarone-3-carboxylic acid respectively. 3-Benzoylcoumaranone-2, however, afforded 2-phenylcoumarone.

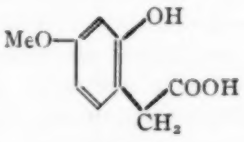
† An account was published in *Exper.*, 1956, **12**, 37.

* The acid has also been synthesised recently by Geismann and Armen (*J. Amer. Chem. Soc.*, 1955, **77**, 1623) who have worked on a related but significantly different topic.

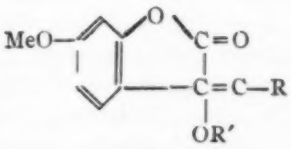
6-Methoxy*iso*coumaranone (X) (Hromatka, *Ber.*, 1942, **75**, 123) has now been conveniently prepared from 2-hydroxy-4-methoxybenzaldehyde by azlactonisation (Robertson, *J. Chem. Soc.*, 1933, 493), hydrolysis by baryta to 2-hydroxy-4-methoxyphenylpyruvic acid, followed by oxidation with hydrogen peroxide to the acetic acid (XI), and then cyclisation by distillation. 6-Methoxycoumaranone-2 proved chemically similar to *iso*coumaranone itself, except that its reactivity was less pronounced. The compound was acylated by acetic anhydride and sodium acetate to (XII : R=Me ; R′=COMe) ; by propionic anhydride and sodium propionate to (XII : R=Et ; R′=COEt) and by benzoic anhydride and sodium benzoate to 6-methoxy-3-benzoylcoumaranone-2 (XII ; R=Ph ; R′=H). The self-condensation of 6-methoxycoumaranone-2 was brought about with sodium hydride yielding (I : R=H ; R′=OMe). The infra-red spectrum of this compound is consistent with this structure. This compound underwent rearrangement in quantitative yield to (XII : R′=Me ; R′=COMe) with acetic anhydride and sodium acetate (cf. Part VI, *loc. cit.*). As expected, the ultraviolet absorption curves of the acyl derivatives (XII : R=Me ; R′=H), (XII, R=Ph ; R′=H) and (I, R=H ; R′=OMe) were similar.



(X)



(XI)



(XII)

* EXPERIMENTAL *

Enolic Methyl Ether of 3-o-*Methoxyphenylacetylcoumaranone-2* (I : R=Me ; R′=H).—Excess of diazomethane (*ca.* 4*M*) was added to an ethereal suspension of the self-condensation product of *iso*coumaranone (1 *M*) and the reaction mixture left in the cold overnight. The sticky mass left on removal of the solvent furnished a crystalline product (yield, 30-35%) on trituration with methanol. The compoudd was washed with dilute alkali and crystallised from methanol in colorless crystalline mass, m.p. 104°, exhibiting a negative ferric reaction. (Found : C, 73.6 ; H, 5.6. $C_{18}H_{16}O_4$ requires C, 73.0 ; H, 5.4%).

2-o-*Methoxybenzylcoumarone-3-carboxylic Acid.*—A solution of the foregoing enolic ether (0.6 g.) in acetic acid (3 c.c.) was boiled with HCl (conc., 1 c.c.) for 3 hours and the product precipitated with water. The greenish semi-solid mass was dried, dissolved in benzene-petroleum ether and the solution allowed to evaporate spontaneously in a refrigerator, when apparently two types of crystals were obtained which were easily separated : (*a*) greenish prisms, m.p. 145° and (*b*) colorless prisms, m.p. 154° ; mixed m.p. of both the samples was 145-54°, indicating that the sample, m. p. 154°, was purer. This on recrystallisation from acetic acid was obtained in colorless prisms, m.p. 157°, giving a negative ferric reaction. (Found : C, 72.1 ; H, 4.9. $C_{17}H_{14}O_4$ requires C, 72.3 ; H, 5.0%). The compound imparted a violet colour to sulphuric acid.

* All m.p.'s are uncorrected

Methylation of (II: R=R′=H).—If the acid is methylated in sodium carbonate solution with methyl sulphate, the product obtained in good yield is methyl 2-*o*-hydroxybenzylcoumarone-3-carboxylate, m.p. 130°, underpressed on admixture with an authentic specimen. (Found: C, 72.2; H, 5.0. Calc. for $C_{17}H_{14}O_4$: C, 72.3; H, 5.0%). When the methylation is done with excess of methyl sulphate and alkali on the water-bath, the alkaline layer filtered and acidified, *2-o-methoxybenzylcoumarone-3-carboxylic acid* was obtained (58% yield), crystallising from acetic acid in colorless prisms, m.p. 157·5°, underpressed on admixture with the sample obtained above. (Found: C, 72.2; H, 5.0. $C_{17}H_{14}O_4$ requires C, 72.3; H, 5.0%). *U. V. absorption*: Continuous absorption in the U. V. region without exhibiting a maxima or minima. *Infra-red spectrum*: λ_{nujol}^{max} 6·05s, 6.25s (COOH), 6.8s (CH_2) and 8-9.0s (ether)μ.

7-Methoxy-β-brazanquinone.—The above acid (0.6 g.) was converted into the acid chloride with thionyl chloride (1.2 c.c.) in CS_2 solution. After removing the solvent, the oily acid chloride was dissolved in CS_2 (12 c.c.) and treated with $AlCl_3$ (0.9 g.) when a yellow aluminium complex separated. The mixture was left overnight, solvent removed by decantation and the residue treated with iced HCl. A semi-solid product (yield > 100%) was obtained which gave a typical Berlin blue colour with sodium hydroxide and chloroform and coupled with diazonium salts to yield azo colours. As the compound was found difficult to purify, the crude material (0.4 g.) in acetic acid (6 c.c.) was oxidised by boiling with chromic acid (0.6 g.) in a small quantity of water. After the exothermic reaction was over (½ min.), the *quinone* (V) (0.2 g.) was isolated as usual and crystallised from acetic acid in yellow prisms, m.p. 242°. It developed a purple colour with sulphuric acid. (Found: C, 73.1; H, 3.8. $C_{17}H_{10}O_4$ requires C, 73.6; H, 3.6%).

β-Brazan.—The above quinone (0.1 g.) was boiled vigorously with HI (6 c.c.) for 2 hours. The crystalline product that condensed on the walls of the condenser was collected from time to time (2-4 mg.) and was identified by determination of m.p. and mixed m.p. The residue in the flask contained dirty phenolic materials which were not investigated.

7-Methoxy-β-brazan.—A mixture of 7-keto-7:8:9:10-tetrahydro-β-brazan (1.8 g., this *Journal*, 1953, **30**, 103), N-bromosuccinimide (0.9 g.) and a few crystals of benzoyl peroxide in chloroform (25 c.c.) was refluxed for 6 hours. The product, worked up in the usual manner, was warmed with pyridine (5 c.c.) for 20 minutes on the water-bath. The mixture was acidified and the crude 7-hydroxy-β-brazan collected and purified by extraction with alkali. The phenol (0.9 g.) was methylated by refluxing in acetone (20 c.c.) with methyl iodide (1 c.c.) and dry potassium carbonate (5 g.) for 6 hours. The *methyl ether*, obtained in quantitative yield, was purified by sublimation and obtained in pointed blades, m.p. 170°. The compound dissolved in sulphuric acid giving a yellow solution, turning blue and finally green. (Found: C, 82.0; H, 4.9. $C_{17}H_{12}O_2$ requires C, 82.2; H, 4.8%). On vigorous boiling with HI this compound gave a small quantity of β-brazan.

This compound on oxidation with chromic acid in acetic acid in the usual manner afforded a yellow quinone, m.p. 245-46° after purification by sublimation. This compound is presumably 7-methoxy-β-brazanquinone, but the determination of mixed m.p.

with the quinone, m.p. 242° described above, could not be carried out due to the loss of the latter by accident. With H_2SO_4 the compound developed a purple colour.

2-o-Hydroxybenzylcoumarone-3-carboxylic Acid Lactone (VI).—The acid (II: R=R'=H) (0.2 g.) was boiled with purified thionyl chloride (2 c.c.) till the crystals went into solution, and then left for 2 hours. Thionyl chloride was removed in vacuum leaving a gum which crystallised on trituration with alcohol. The lactone crystallised from alcohol in colorless prisms, m.p. 138°, undepressed on admixture with a specimen prepared with the aid of propionic anhydride. (Found: C, 76.7; H, 4.0. Calc. for $C_{16}H_{10}O_3$: C, 76.8; H, 4.0%).

Wolff-Kishner Reduction of 2-o-Hydroxybenzoylcoumarone-3-carboxylic Acid Lactone.—A mixture of the lactone (0.2 g., this *Journal*, 1955, **32**, 265), KOH (0.6 g) and hydrazine hydrate (1 c.c., 80%) was refluxed for 1½ hours; water was removed from the system by distillation and then the mixture heated at 200-205° for 3½ hours. The dark solution was diluted with water (charcoal), filtered, acidified and the resulting solid crystallised from acetic acid. The product appeared to be the corresponding *azine* which was obtained in colorless plates, m.p. > 300°, exhibiting a yellow coloration with H_2SO_4. (Found: C, 69.1; H, 3.9. $C_{32}H_{20}O_6N_2$ requires C, 68.6; H, 3.6%).

Keto-nitrile (IX).—A mixture of *o*-methoxyphenylacetonitrile (3.0 g.), sodium hydride (0.95 g.) and ethyl acetate (4 c.c.) in benzene (30 c.c.) was refluxed for 4 hours after the addition of a drop of alcohol. The *sodium salt* of the keto-nitrile separated. The *nitrile* (2.9 g.), worked up in the usual manner, was obtained in prisms, m.p. 84-85° from acetic acid. (Found: C, 70.5; H, 5.8. $C_{11}H_{11}O_2N$ requires C, 69.8; H, 5.8%).

2-Methylcoumarone-3-carboxylic Acid.—(*a*). A mixture of the foregoing keto-nitrile (8.0 g.), acetic acid (60 c.c.) and HBr (50 c.c., 48%) was refluxed for 5 hours. The mixture was cooled, diluted with water and extracted with ether (3 × 30 c.c.). The ethereal layer was washed with dilute alkali and the alkaline layer acidified to afford the *carboxylic acid* (0.4 g.) which crystallised from aqueous alcohol in colorless plates, m.p. 191-91.5° (lit., m.p. 191°). (Found: C, 68.0; H, 4.6. Calc. for $C_{10}H_8O_3$: C, 68.2; H, 4.5%). The *amide* crystallised from alcohol in colorless needles, m.p. 179°, showing no coloration with H_2SO_4. (Found: C, 68.2; H, 4.7. $C_{10}H_9O_2N$ requires C, 68.6; H, 5.1%).

The above neutral ethereal solution was dried (Na_2SO_4) and the solvent removed. The pale yellow oily residue furnished 2-methylcoumarone (1.5 g.) on distillation (b.p. 191°/760 mm). The high boiling residue in the distilling flask was dissolved in acetic acid (5 c.c.) and left overnight when a solid separated (*ca.* 1 g.). This crystallised from benzene-petroleum ether in colorless prisms, m.p. 168-69°. The compound gave a violet-red colour with H_2SO_4 and appeared to be a polymeride of 2-methylcoumarone. [Found: C, 81.1, 81.7; H, 6.1, 6.2. $(C_9H_8O)_n$ requires C, 81.8; H, 6.1%].

(*b*). A mixture of 3-acetylcoumaranone-2 (0.5 g.), acetic acid (6 c.c.) and HCl (4 c.c.) was boiled for 6 hours. The colorless solution was poured into water and the crystalline product collected and crystallised from aqueous alcohol in colorless plates, m.p. 191-92°, showing a negative ferric reaction. (Found: C, 68.4; H, 4.6. Calc. for $C_{10}H_8O_3$: C, 68.2; H, 4.5%).

2-*Ethylcoumarone-3-carboxylic acid* was similarly prepared as above from 3-propionylcoumaranone-2. The *acid* crystallised from aqueous alcohol in colorless needles, m.p. 115°. (Found : C, 69.8 ; H, 5.1. $C_{11}H_{10}O_3$ requires C, 69.5 ; H, 5.3%).

6-*Methoxy-2-methylcoumarone-3-carboxylic acid* was similarly prepared with the aid of HCl from (XII : R=Me ; R′=COMe) (preparation given below). The *acid* crystallised from aqueous alcohol in pinkish plates, m.p. 196°. (Found : C, 63.8 ; H, 4.9. $C_{11}H_{10}O_4$ requires C, 64.1 ; H, 4.8%).

2-*Phenylcoumarone* was obtained by boiling 3-benzoylcoumaranone-2 with HCl in acetic acid for 8 hours. The compound crystallised from alcohol in colorless plates, m.p. and mixed m.p. 120°.

6-*Methoxy*iso*coumaranone* (X).—The azlactone (20 g., m.p. 150°), derived from 2-hydroxy-4-methoxybenzaldehyde (Robertson, *loc. cit.*), was hydrolysed by refluxing for 24 hours with a mixture of hydrated barium hydroxide (45 g.), alcohol (45 c.c.) and water (200 c.c.). The *barium salt* was collected, washed with water and decomposed with hydrochloric acid. 2 *Hydroxy-4-methoxyphenylpyruvic acid* was obtained which crystallised from acetic acid in small prisms, m.p. 154-55° (gas evolution), developing a bluish colour with ferric chloride. (Found : C, 57.2 ; H, 4.8. $C_{10}H_{10}O_5$ requires C, 57.1 ; H, 4.8%). If the above hydrolysis is done for 8 hours and the barium salt worked up, a mixture of the above α-ketonic acid and the *azlactonic acid* is obtained ; the latter crystallises from aqueous acetic acid in colorless prisms, m.p. 217° (frothing). The compound showed no ferric reaction. (Found : C, 64.9 ; H, 5.1. $C_{17}H_{15}O_5N$ requires C, 65.2 ; H, 4.8%). When NaOH is employed in place of baryta, the isolation of the products becomes very difficult (cf. Jatzkewitz and Offe, *Chem. Ber.*, 1947, **80**, 474).

The ketonic acid (12.0 g.) was dissolved in aqueous NaOH (100 c.c., 10 %) and treated at 0°-5° with hydrogen peroxide (15 c.c., 30%). The mixture was left overnight, acidified with HCl and extracted with ether (4 × 30 c.c.). 2-Hydroxy-4-methoxyphenylacetic acid was obtained on removal of the ether (yield, 5.5 g.). This crystallised from alcohol-benzene as cream-coloured prisms, m.p. 130° (lit., m.p. 130°).

The acid (5.0 g.) was fractionated in vacuum when the colorless distillate (3.3 g.) immediately solidified, furnishing 6-methoxy*iso*coumaranone, m. p. 55-56°. (Found : C, 65.5 ; H, 4.8. Calc. for $C_9H_8O_3$: C, 65.8; H, 4.9%). Hromatka (*loc. cit.*) records m.p. 56°.

Self-condensation of 6-*Methoxy*iso*coumaranone*.—A solution of the *iso*coumaranone (1.6 g.) in benzene (10 c.c.) was added to a suspension of sodium hydride (0.26 g.) in benzene (5 c.c.) and the mixture refluxed for 6 hours. The *sodium salt* of the self-condensation product began to separate after 1 hour. The mixture was then cooled and carefully decomposed with water and the aqueous layer acidified to furnish 3-(2-*hydroxy-4-methoxyphenylacetyl*)-6-*methoxycoumaranone*-2 (1.1 g.). The compound showed a bluish green ferric reaction and crystallised from acetic acid in thick plates, m.p. 169°. (Found : C, 65.5 ; H, 4.7. $C_{18}H_{16}O_6$ requires C, 65.8 ; H, 4.9%). The compound was soluble in sodium bicarbonate and developed a deep blue coloration with H_2SO_4. *U. V. absorption* : λ^{max}_{MeOH} 3500Å (log ε, 3.63), 3235Å (log ε, 4.27). *Infra-red spectrum* : λ^{max}_{nujol} 3.2s (OH phenolic), 3.4s (OH hydrogen bonded), 5.80s (lactone carbonyl), 6.07s, 6.14s (double bond), 8-9.0s (ether)μ.

The *diacetyl* derivative was obtained by boiling the compound with acetic anhydride for 1½ hours. It crystallised from alcohol in drab needles, m.p. 162-63°. (Found : C, 64.6; H, 4.8. $C_{22}H_{20}O_8$ requires C, 64.1 ; H, 4.8%). The compound showed no ferric reaction and was insoluble in cold dilute alkali.

6-*Methoxy*-3-*acetylcoumaranone*-2.—6-Methoxy*iso*coumaranone or its self-condensation product (0.5 g.) was refluxed with acetic anhydride (6 c.c.) and sodium acetate (0.3 g.) for 1½ hours and the mixture poured into water. The enolic *acetyl* derivative of 6-methoxy-3-acetylcoumaranone-2 (0.5 g.) was obtained which crystallised from acetic acid in slightly brownish needles, m. p. 143°, insoluble in sodium bicarbonate. (Found : C, 62.8 ; H, 5.0. $C_{13}H_{12}O_5$ requires C, 62.9; H, 4.8%). This acetyl derivative was shaken for 2½ hours with an excess of sodium carbonate solution (15%) at 60°. The aqueous solution was clarified with charcoal and acidified. The brown precipitate of 6-*methoxy*-3-*acetylcoumaranone*-2 crystallised from acetic acid in cream-coloured prisms, m.p. 148°, exhibiting a deep blue ferric reaction. (Found : C, 64.2 ; H, 5.0. $C_{11}H_{10}O_4$ requires C, 64.1 ; H, 4.9%). *U. V. absorption* : λ^{max}_{MeOH} 3400Å (log ε, 3.92).

Propionyl Derivative of 6-*Methoxy*-3-*propionylcoumaranone*-2.—A mixture of 6-methoxy*iso*coumaranone (0.3 g.), propionic anhydride (1 c.c.) and sodium propionate (0.2 g.) was heated on the water-bath for 2 hours and then poured into a cooled potassium carbonate solution. The crystalline *product* (0.2 g.) crystallised from alcohol in brownish plates, m.p. 74-75°. (Found : C, 65.5 ; H, 5.7. $C_{15}H_{16}O_5$ requires C, 65.2 ; H, 5.8%).

6-*Methoxy*-3-*benzoylcomaranone*-2.— A mixture of 6-methoxy*iso*coumaranone (0.35 g.), benzoic anhydride (1.4 g.) and sodium benzoate (0.5 g.) was heated at 175° for 2 hours and then water was added to the cooled mixture. Benzene (5 c.c.) and aqueous sodium carbonate solution (10 c.c., 10%) were added to the mixture and shaken mechanically for 3 hours at 45°. The aqueous layer was removed, acidified and the mixture warmed till benzoic acid just dissolved, and the crystalline residue filtered quickly. 6-*Methoxy*-3-*benzoylcoumaranone*-2 (0.35 g.) was crystallised from methanol and obtained in yellowish needles, m.p. 116°. The compound showed a deep blue ferric reaction. (Found : C, 71.7 ; H, 4.4. $C_{16}H_{12}O_4$ requires C, 71.6 ; H, 4.5%). *U. V. absorption*: λ^{max}_{MeOH} 3450Å (log ε, 3.98).

Isomerisation of the Self-condensation Product.—The above mentioned self-condensation product of 6-methoxy*iso*coumaranone (0.3 g.) was dissolved in acetic acid (5 c.c.) and boiled with HCl (1.5 c.c.) for 3 hours and then poured into water. 6-*Methoxy*-2-(2-*hydroxy*-4-*methoxybenzyl*)-*coumarone*-3-*carboxylic acid* (II : R=H ; R′=OMe) (1.0 g.) was obtained as a gum which soon solidified. The compound separated from acetic acid in brownish needles, m.p. 190-92°. (Found : C, 65.2 ; H, 4.8. $C_{18}H_{16}O_6$ requires C, 65.9 ; H, 4.9%). The compound showed a pink colour with H_2SO_4.

The author wishes to thank the Ministry of Education, Government of India and the authorities of Patna University for generous grants. The U. V. and I. R. spectra were kindly determined by Dr. G. Baker and Mr. H. M. Ghosh of the State College Montana.

CHEMICAL LABORATORY,
SCIENCE COLLEGE, PATNA-5.

Received November 3, 1956.

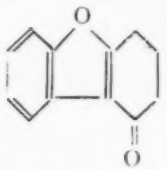
[Jour. Indian Chem. Soc., Vol. 34, No. 4, 1957]

EXPERIMENTS ON THE SYNTHESES OF FURANO COMPOUNDS. PART XIII. 1-SUBSTITUTED DIBENZOFURANS

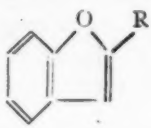
By J. N. Chatterjea

The cyclic ketone (I) has been synthesised and converted into some difficultly accessible 1-substituted dibenzofurans.

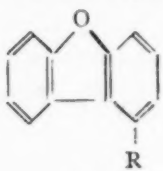
It has been shown in an earlier communication that the Kipping cyclisation may be effected at the 3-position of benzofurans yielding cyclic ketones (this *Journal*, 1955, **32**, 265). It is of interest to synthesise the simple ketone (I) as a source of 1-substituted dibenzofurans because as yet neither any reaction has been found which permits the direct substitution in 1-position of dibenzofuran nor any 1-monosubstituted derivative has been prepared by direct ring-closure—these derivatives being usually accessible only by indirect methods (Gilman and Van Ess, *J. Amer. Chem. Soc.*, 1939, **61**, 1365).



(I)



(II : R = $CO.CH_2Br$)
(III : R = $COCH_2.CH_2$ COOH)
(IV : R = $CH_2.CH_2.CH_2.COOH$)



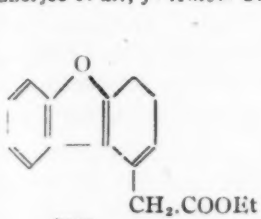
(V)

2-Bromoacetylcoumarone (II) (Shriner and Anderson, *ibid.*, 1939, **61**, 2705) was converted by the usual malonic ester synthesis to the keto-acid (III) and thence to the butyric acid (IV) by the Wolff-Kishner reduction. The latter, purified through the methyl ester, was cyclised in good yield to (I) by way of the acid chloride with the aid of stannic chloride. This ketone was converted into dibenzofuran by reduction with $LiAlH_4$ to the nicely crystalline carbinol (I : CHOH in place of CO) followed by dehydrogenation with palladised charcoal or by reduction to 1 : 2 : 3 : 4-tetrahydrodibenzofuran and then dehydrogenation with *N*-bromosuccinimide.

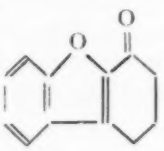
Dehydrogenation of the ketone (I) with N-bromosuccinimide furnished the known 1-hydroxydibenzofuran (V : R = OH ; Gilman and Van Ess, *loc. cit.* ; Van Ess *et al.*, *Chem. Abs.*, 1938, **32**, 4161). By reaction with methylmagnesium iodide in the usual way, the ketone was converted into the new 1-methyldibenzofuran* (V, R = Me) which furnished the acid (V : R = COOH ; Van Ess, *Chem. Abs.*, 1938, **32**, 4981 ; Hogg, *ibid.*, 1946, **40**, 4716) by oxidation. The oxime of the ketone (I) on reduction with sodium amalgam or by $LiAlH_4$ (cf. Walter, *J. Amer. Chem. Soc.*, 1952, **47**, 5185) gave 1-amino-1 : 2 : 3 : 4-tetrahydrodibenzofuran. Preliminary experiments indicate that the compound may be dehydrogenated 1-aminodibenzofuran. A Reformatsky reaction with (I) and

*Trippett (*J. Chem. Soc.*, 1957, 419) has now prepared it in an impure state.

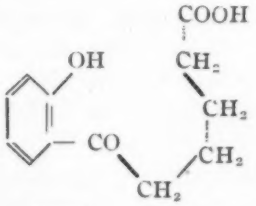
ethyl bromoacetate afforded the ester (VI) which, on attempted dehydrogenation with palladised charcoal, gave exclusively 1-methyldibenzofuran by decomposition (cf. Banerjee *et al.*, *J. Amer. Chem. Soc.*, 1955, **77**, 408).



(VI)



(VII)



(VIII)

On general grounds, it may be expected that the tetrahydrodibenzofuran on oxidation with chromic acid would yield the ketone (VII ; cf. Johnson *et al.*, *ibid.*, 1944, **66**, 219). The sole product of oxidation, carried out in acetic acid, was, however, *o*-hydroxybenzoylvaleric acid (VIII), previously obtained by others from hexahydrodibenzofuran by oxidation (von Braun, *Ber.*, 1922, **55**, 3767 ; Ebel, *Helv. Chim. Acta*, 1929, **12**, 10). Attempted hydroxylation of the tetrahydro compound by selenium dioxide in acetic acid resulted only in dehydrogenation to dibenzofuran. This line of work was not pursued further when our notice was drawn to a preliminary announcement of Winternitz and Lachazette (*Bull. soc. chim.*, 1955, 1393) who obtained fruitful results in this direction.†

*Experimental

β-2-Benzofuroylpropionic Acid (III).—Ethyl sodiomalonate, prepared from sodium (4.6 g.) and ethyl malonate (32.0 g.), in benzene (250 c.c.) was cooled and treated with a solution of 2-bromoacetylcoumarone (36 g.) in benzene (100 c.c.) and then refluxed for 4 hours, cooled, treated with water and washed with brine (to avoid emulsions). Benzene was removed in vacuum and the thick brown oily residue hydrolysed by refluxing with alcoholic potash (KOH 40 g., alcohol 60 c.c. and water 140 c.c.) for 1 hour. After removing alcohol by distillation, water (150 c.c.) was added to the residue, filtered from the brown sludge and acidified to provide a dirty precipitate of the *malonic acid* which was best purified by washing with cooled ethyl acetate-petroleum ether. This acid crystallised from ethyl acetate-petroleum ether in slender prismatic needles, m.p. 178° (decomp.), yield 18-20 g.

Decarboxylation of the acid (1.8 g.) at 180° was complete in 10 minutes ; the residue was then extracted with sodium bicarbonate, clarified with charcoal and acidified to afford the *propionic acid* (III) (1.2 g.) which was obtained from aqueous alcohol in cream-coloured crystalline mass, m.p. 140° (yield of the pure compound, 1.0 g.). (Found : C, 65.5 ; H, 4.6. $C_{12}H_{10}O_4$ requires C, 66.0 ; H, 4.6%).

γ-2-Benzofurylbutyric Acid (IV).—A mixture of the above propionic acid (10 g.), purified diethyleneglycol (62 c.c.), hydrazine hydrate (10 c.c., 85%) and KOH (9 g.) was refluxed for ½ hour ; water was removed from the system by distillation and then the temperature raised to 200°-210° and maintained there for 3 hours. The mixture was

†For details see *Bull. Soc. Chim.*, 1956, 1817

All M. P.'s are uncorrected.

cooled, diluted with water and acidified. The *butyric acid* was obtained as a dark crystalline precipitate (8.5 g.). This was converted into the *methyl ester* by refluxing in dry methanolic solution containing 10% sulphuric acid. On distillation the ester was obtained as a homogeneous, colorless, mobile liquid, b.p. 145-48°/2.5 mm (yield, nearly quantitative). On hydrolysis with alcoholic sodium hydroxide for ½ hour, the acid was obtained as snow-white crystals, crystallising from benzene-petroleum ether in colorless prisms, m.p. 82-83°. (Found: C, 70.5; H, 6.0. $C_{12}H_{12}O_3$ requires C, 70.6; H, 5.9%).

1-*Keto*-1:2:3:4-*tetrahydrodibenzofuran* (I).—The foregoing acid (8.4 g.) was converted into the acid chloride by boiling with thionyl chloride (10 c.c.) for 5 minutes and then excess of thionyl chloride removed completely in vacuum. The oily acid chloride was dissolved in CS_2 (30 c.c.), cooled and treated with $SnCl_4$ (14 g.) when a crystalline complex at once separated. After 3 hours, CS_2 was decanted off, the residue decomposed with iced HCl, the whole extracted with ether and the ethereal layer washed with sodium bicarbonate. The oily residue after removal of the solvent on distillation furnished the *ketone* (I) at 160-64°/2-3 mm; yield 4.1 g. (Found: C, 77.5; H, 5.6. $C_{12}H_{10}O_2$ requires C, 77.4; H, 5.4%). The viscous residue in the distilling flask on dissolving in acetone deposited crystals (*ca.* 2 g.), sparingly soluble in alcohol, acetic acid but soluble in chloroform and benzene. Crystallised from chloroform-acetone, this was obtained in thick plates, m.p. 216-19°. The compound was insoluble in boiling alkali and contained sulphur.

The 2:4-*dinitrophenylhydrazone* of the above ketone crystallised from acetic acid in long orange needles, m.p. 276° (decomp.). (Found: N, 15.5. $C_{18}H_{14}O_5N_4$ requires N, 15.3%). The *oxime* crystallised from methanol in colorless rectangular prisms, m.p. 143°. (Found: N, 7.3. $C_{12}H_{11}O_2N$ requires N, 7.0%).

Dibenzofuran.—A solution of $LiAlH_4$ (50 mg.) in ether (20 c.c.) was added to a solution of the ketone (I: 0.1 g.) in ether (10 c.c.). After ½ hour, the solution was decomposed with HCl (dil.) and the ethereal layer on evaporation afforded a quantitative yield of 1-*hydroxy*-1:2:3:4-*tetrahydrodibenzofuran*, crystallising from benzene-petroleum ether in colorless fluffy needles, m.p. 109-10°. (Found: C, 76.8; H, 6.5. $C_{12}H_{12}O_2$ requires C, 76.6; H, 6.4%).

On dehydrogenation at 300° with palladised charcoal for 2 hours, the above carbinol afforded dibenzofuran, m.p. and mixed m.p. 86°.

1-*Methyldibenzofuran* (V: R = Me).—A solution of the ketone (I: 0.5 g.) in ether (5 c.c.) was added to an excess of ethereal methylmagnesium iodide and refluxed for 1 hour. The product on working up in the usual manner was dried and heated in a metal bath with palladised charcoal (0.3 g.) at 280° for 2 hours and distilled in vacuum. 1-*Methyldibenzofuran* was obtained as a colorless mobile liquid (0.2 g.), b.p. 125°/1.2 mm, having a characteristic odour. (Found: C, 85.3; H, 5.9. $C_{13}H_{10}O$ requires C, 85.7; H, 5.5%). The *picrate* separated from picric acid solution as orange plates, m.p. 58° (with shrinking). (Found: N, 10.6. $C_{13}H_{13}O.C_6H_3O_7N_3$ requires N, 10.3%).

Dibenzofuran-1-carboxylic acid was obtained by oxidising the material (0.1 g.) with $KMnO_4$ (50 c.c., 2%) for 36 hours. The acid was obtained in colorless leaflets, m.p. 232-33° (lit., m.p. 232°). (Found: C, 73.0; H, 4.0. Calc. for $C_{13}H_8O_3$: C, 73.1; H, 3.9%). The methyl ester prepared with diazomethane was obtained in prismatic needles, m.p. 63° (lit., m.p. 63°).

1-*Hydroxydibenzofuran* (V: R=OH).—A mixture of the ketone (I: 0.45 g.), *N*-bromosuccinimide (0.43 g.), benzoyl peroxide (*ca.* 1 mg.) in CCl_4 (10 c.c.) was refluxed for 6 hours. The mixture was cooled, filtered to remove succinimide, solvent removed by distillation, the residue treated with pyridine (5 c.c.) and warmed on the water-bath for ½ hour. The mixture was acidified, extracted with ether and the ethereal solution extracted with alkali (2 × 10 c.c., 5%). The greenish solution on acidification gave a crystalline precipitate of the phenol (V: R=OH) (0.22 g.), which crystallised from benzene in prisms, m.p. 141° (lit., m.p. 140.5°). (Found: C, 78.5; H, 4.1. Calc. for $C_{12}H_8O_2$: C, 78.3; H, 4.4%).

The *acetyl* derivative crystallised from alcohol in cream-coloured prisms, m.p. 76°. (Found: C, 73.9; H, 4.3. $C_{14}H_{10}O_3$ requires C, 74.3; H, 4.4%).

1-*Amino*-1:2:3:4-*tetrahydrodibenzofuran*.—(*i*). A solution of the oxime (0.8 g.) of the ketone (I) in absolute alcohol (30 c.c.) was gradually treated at 50° with sodium amalgam (total, 25 g., 2%) and the system maintained acidic by periodic addition of acetic acid. Sodium acetate separated quickly. The whole was diluted, acidified, filtered from unchanged oxime and the filtrate extracted with ether to remove the unchanged material. The acidic layer on basification afforded the *amine* which was isolated with ether and obtained as an oil with characteristic basic odour. This was dissolved in dry ether (15 c.c.) and dry hydrogen chloride passed into the solution. The precipitated *hydrochloride* crystallised from alcohol-ether in colorless needles (0.2 g.), m.p. 233-34°. (Found: Cl, 16.8. $C_{12}H_{13}ON.HCl$ requires Cl, 15.9%).

(*ii*). An excess of $LiAlH_4$ (0.2 g.) was added to a solution of the oxime (0.3 g.) in ether (15 c.c.). The mixture was left overnight at the room temperature and then worked up as above to provide the amine (yield 35%). On heating with palladised charcoal, the product was found to contain some 1-aminodibenzofuran by diazo coupling test.

Condensation of Ethyl Bromoacetate with 1-*Keto*-1:2:3:4-*tetrahydrodibenzofuran*.—Ethyl bromoacetate (1.5 g.) was condensed with the ketone (1.8 g.) in benzene (25 c.c.) solution in the presence of activated zinc dust. The reaction (sluggish) was initiated with a few crystals of iodine. The mixture was refluxed for 24 hours, treated with fresh zinc (1 g.) and left further for 24 hours. The yellowish mixture was decomposed with HCl, extracted with benzene, washed with dilute ammonia, dried ($MgSO_4$) and the solvent removed. The viscous residue (1.8 g.) was warmed for ½ hour with formic acid (5 c.c., 98-100%), diluted with water, extracted with ether and the ethereal solution washed with sodium bicarbonate solution and the solvent removed completely. The thick viscous residue of (VI: 1.2 g.) was dried, mixed with palladised charcoal (0.1 g.), dehydrogenated at 240-80° for 2 hours and distilled in vacuum. The main product (1.0 g.) distilled at 130-32°/1.5 mm and identified as 1-methyl-

dibenzofuran by analysis and by direct comparison of the picrate. (Found : C, 85.6 ; H, 5.6. $C_{13}H_{10}O$ requires C, 85.7 ; H, 5.5%). The residue in the flask gave on hydrolysis a negligible quantity of an acidic material.

1 : 2 : 3 : 4-*Tetrahydrodibenzofuran* was prepared from the ketone (I) by reduction (Huang-Minlon procedure) in the usual manner. The compound was purified through the picrate (cf. Cullinane and Padfield, *J. Chem. Soc.*, 1935, 1131). The compound was, however, prepared in quantity by the catalytic reduction of dibenzofuran in acetic acid in presence of Adams' catalyst (cf. Cullinane *et al.*, *loc.cit.*).

Oxidation of Tetrahydrodibenzofuran : (*i*) *With Chromic Acid.*—A solution of the compound (2.5 g.) in acetic acid (15 c. c.) was treated at 0° with a solution of chromic acid (2.5 g.) in water (2 c. c.) and the mixture left in the refrigerator for 24 hours. No ketone could be detected in that mixture. After leaving for 4 days at the room temperature, the mixture was worked up to give an acidic material (0.5 g.), crystallising from acetic acid in prismatic needles, m.p. 94°, and identified as *o*-hydroxybenzoylvaleric acid (VIII). (Found : C, 65.0 ; H, 6.5. Calc. for $C_{12}H_{14}O_4$: C, 64.9 ; H, 6.3 %).

(*ii*) *With Selenium Dioxide.*—A mixture of the compound (1.7 g), acetic acid (11 c. c.), water (0.5 c.c.) and selenium dioxide (1.1 g.) was refluxed for 5 hours. Selenium separated rapidly and quantitatively. The solution was filtered and steam-distilled when some unchanged product and dibenzofuran (m.p. 86°) were obtained. The dark sticky residue proved unprofitable to work up.

(*iii*) *With N. B. S.*—The product of oxidation with *N*-bromosuccinimide in CCl_4 in presence of benzoyl peroxide was dibenzofuran (purified by steam-distillation) and some halogenated material.

3-*Chloroacetylcoumarone* was prepared with a view to synthesising β-3-benzofuroylpropionic acid. Reichstein's benzofuran-3-carboxylic acid (*Helv. Chim. Acta*, 1937, **20**, 883) was converted into the acid chloride and to the corresponding diazo-ketone (Reichstein *et al.*, *loc.cit.*). A solution of the pure diazo-ketone in ether was decomposed under cooling by ethereal HCl. The *chloroketone* (70% yield based on diazo-ketone) crystallised from alcohol in cream-coloured needles, m.p. 142-43°. (Found : C, 61.9 ; H, 3.6. $C_{10}H_7O_2Cl$ requires C, 61.7 ; H, 3.6 %). Preliminary experiments on condensation with malonic ester have not given encouraging results.

CHEMICAL LABORATORY,
SCIENCE COLLEGE, PATNA-5.

Received November 3, 1956.

[Jour. Indian Chem. Soc., Vol. 35, No. 4, 1957]

STUDIES ON THE METAL COMPLEXES OF HYDROXAMIC ACIDS. PART I. SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE WITH NICOTINO- AND *iso*NICOTINOHYDROXAMIC ACIDS

By R. L. Dutta

Nicotino- and *iso*nicotinohydroxamic acids are proposed as reagents for the spectrophotometric determination of manganese, by making use of the red-violet colour formed by the interaction of the metal with the reagents in ammoniacal medium (at or above p_H 9). The colour intensity is measured at 480-490 mμ for nicotino- and at 470-480 mμ for *iso*nicotinohydroxamic acid. Beer's law is obeyed and the Sandell sensitivities are 0.014 γ for nicotino- and 0.013 γ for *iso*nicotinohydroxamic acid. Job's method indicates 1 : 3 complex between the metal and the reagents. In the coloured products, manganese is believed to be in tervalent state. Copper, nickel, cobalt, silver and iron interfere seriously in the estimation of manganese. However, the first four interfering metals can be masked by sodium cyanide.

Picolinohydroxamic acid, curiously enough, exhibits only a faint red-violet colour under the same conditions, but fades rapidly.

Hydroxamic acids, having the group $-\overset{\overset{O}{\|}}{C}-NHOH$ or $-\overset{\overset{OH}{|}}{C}=NOH$, form, in general, strongly coloured complexes with iron, vanadium, uranium and molybdenum. Recently, a few hydroxamic acids have been studied as colorimetric reagents for these metals. Benzohydroxamic acid has been used for the detection and colorimetric estimation of vanadium in 50% alcohol (Dasgupta and Singh, *J. Sci. Ind. Res.*, 1952, **11B**, 268) and also by extraction of the aqueous colour with hexanol (Wise and Brandt, *Anal. Chem.*, 1955, **27**, 1392). Salicylohydroxamic acid has been studied as a colorimetric reagent for vanadium, molybdenum and uranium (Bhaduri and Rây, *Science & Culture*, 1952, **18**, 97), and afterwards also for titanium (Xavier, Chakrabortty and Rây, *ibid.*, 1954, **20**, 146). Oxalohydroxamic acid has been used for indirect colorimetric estimation of zirconium and calcium (Dhar and Das Gupta, *J. Sci. Ind. Res.*, 1952, **11B**, 500, 520). Although a few hydroxamic acids have been studied, these studies are far from exhaustive. With a view to finding out more sensitive and effective reagents for the colorimetric estimation of metals, a systematic study on the coloured complexes of different metals with pyridine-hydroxamic acids was undertaken.

Nicotino- and *iso*nicotinohydroxamic acids have been found to develop intense red-violet colour with traces of manganese in ammoniacal medium, which is highly sensitive and useful for the estimation of the metal. On the other hand, with picolinohydroxamic acid, a faint red-violet colour appears only on prolonged agitation and this colour is very much unstable and fades away with precipitation of manganic hydroxide. An account of the spectrophotometric determination of manganese with nicotino- and *iso*nicotinohydroxamic acids is reported in the present

communication. Das Gupta and Singh (*loc. cit.*) have studied the reaction between manganese and benzohydroxamic acid in a qualitative manner.

When nicotino- and *iso*nicotinohydroxamic acids are added to an extremely small amount of manganese and the medium is made ammoniacal, there develops an intense red-violet colour. In place of ammonia, caustic soda, methylamine, ethylamine or ethanolamine may be used, but ethylenediamine appears to have a masking effect on manganese. However, ammonia was preferred, because, in its presence, the coloured product was found to be the most stable and also because of its forming soluble complexes with many inorganic cations. The coloured products do not attain their maximum intensity immediately except in presence of excess reagents and at a p_H of or above 9. The maximum absorption regions of the colour are at 480-490 mμ for nicotino- and 470-480 mμ for *iso*nicotinohydroxamic acids, where the reagent solutions have no absorption. For complete colour formation the minimum quantity of the reagent necessary amounts to at least fifteen times the molar proportion of manganese, a very large excess having no adverse effect on the optical density. The coloured products obey Beer's law very closely over the range 0.25 to 10 p.p.m. of manganese. According to Sandell's definition ("Colorimetric Determination of Traces of Metals", 2nd ed., p. 50, Interscience Publishers, Inc., 1950), the sensitivities of the reagents for manganese are 0.014γ per cm^2 for nicotino- and 0.013 γ for *iso*-nicotinohydroxamic acids. The colours are stable at room temperature (20°-30°) and the optical densities remain unchanged at least for a day.

The following observations about the colour appear to be pertinent. The colour is not developed at all in presence of a strong reducing agent, e.g. hydroxylamine or hydrazine. On the other hand, in presence of a trace of hydrogen peroxide, the colour appears immediately, although excess hydrogen peroxide destroys the colour, due probably to the oxidation of the hydroxamic acids. Besides, the colour resembles that of manganic^{III} complexes. Hartmann and Schlafer (*Angew. Chem.*, 1954, **66**, 768) report 475 mμ as the absorption maximum for the Cs-Mn^{III} alum colour. Scheffer and Hammaker (*J. Amer. Chem. Soc.*, 1950, **72**, 2575) report 460 mμ as the absorption maximum of $[MnF_6]^{3-}$ ion. Cartledge and Ericks (*ibid.*, 1936, **58**, 2065) report 520 mμ as the absorption maximum of trioxalato-manganic^{III} ion and 450 mμ as that of diaquo-dioxalato-manganic^{III} ion. All these facts, taken together, strongly support the idea that the coloured complexes in the present case contain presumably tervalent manganese, formed through aerial oxidation of Mn^{II}. The colour is not formed in an atmosphere of carbon dioxide.

Ions like SO_4^{2-}, NO_3^-, Cl^-, SCN^-, CO_3^{2-} $S_2O_3^{2-}$, I^-, Cd^{2+} Zn^{2+}, Al^{3+}, MoO_4^{2-}, WO_4^{2-} etc do not interfere even when present in large amounts. In presence of appreciable amounts of BO_3^{3-}, PO_4^{3-}, tartrate and oxalate, the colour develops slowly and should be measured after 30 minutes. CN^- up to 200γ does not interfere. In presence of vanadium, titanium and uranium, the colour is measured at 540-560 mμ. Interfering effects due to copper, nickel, cobalt and silver can be eleminated by the addition of a little sodium cyanide. Mercury can be masked by an excess of KI. However, iron interferes at all concentrations and should be removed before the determination.

EXPERIMENTAL

A Unicam SP 600 spectrophotometer was used for measuring the optical density of the solutions using Corex glass cells of 1 cm thickness. Measurements of p_H were made with the help of a Cambridge p_H-meter.

A 2% solution of G.R. manganous sulphate was prepared to which a few drops of G.R. H_2SO_4 were added. The manganese content of this solution was determined gravimetrically as pyrophosphate. From this solution, by stepwise dilution, a solution containing 0.05 mg. of Mn was prepared. This solution was used for the spectrophotometric determination of manganese.

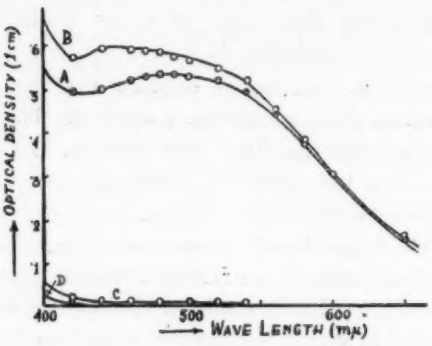
Preparation of the Reagents.—Nicotino- and *iso*nicotinohydroxamic acid hydrochlorides were prepared according to the method outlined by Gardner *et al.* (*J. Amer. Chem. Soc.*, 1951, **73**, 5455). Nicotinic acid and *iso*nicotinic acid (35 g. each) were converted into ethyl esters by following the methods of Laforge (*ibid.*, 1928, **50**, 2479) and of Supriewski and Serafinowna (*Arch. Chem. Farm.*, 1936, **3**, 109). Sodium (12 g.) was dissolved in about 400 c.c. absolute ethyl alcohol (twice distilled over lime and then over sodium). To perfectly dry and finely powdered hydroxylamine hydrochloride (35 g.), taken in a three-necked flask fitted with an efficient mechanical stirrer, was added about 100 c.c. of absolute alcohol and the mixture stirred. The sodium ethoxide solution was now added in small amounts at a time, while stirring was continued for about 1½ hours and was filtered. The filtrate was taken in a flask, treated with the ester (30 g.) and allowed to stand at 20-25° for about 12-16 hours, under constant stirring. This was afterwards evaporated to dryness on the water-bath under reduced pressure and the residue was extracted with boiling ethyl alcohol (500 c.c.) and filtered. Dry HCl gas was passed in the cold, when crystals of the crude hydroxamic acid hydrochloride separated. These were filtered, dissolved in minimum amount of hot water (about 20 c.c.) and then filtered again. To the filtrate was added about 200 c.c. alcohol and the mixture cooled when crystals of the pure hydrochloride separated. These were filtered, washed with alcohol and finally dried in air as shining, almost colorless crystals (m. p. of nicotinohydroxamic hydrochloride 185-86° and that of *iso*nicotinohydroxamic hydrochloride, 206-207°) ; yield 16-20 g.

A freshly prepared 1% reagent solution was used. Solutions of diverse ions were prepared from suitable salts.

Optimum Wave-length for Measurement of the Optical Density of the Colour.—The absorption spectra of the coloured products (Mn content 8 γ per c.c.) in presence of a large excess of the reagents and at a p_H 9 are represented in Fig. 1, together with those of the same amount of the reagent (against water) at the same p_H. It follows from the figure that optimum wave-length for measurement of the optical density is 480-490 mμ for nicotino- and 470-480 mμ for *iso*nicotinohydroxamic acid. At these wave-lengths the reagents have got very little absorption. All subsequent measurements were therefore carried out at these wave-lengths against a reagent blank, having the same amount of the reagent as in the coloured product and the same p_H.

FIG. 1

Absorption spectra of coloured products.



A. Mn-nicotinohydroxamic acid : p_H 9 ; 8 γ Mn/c.c.

B. Mn-*iso*nicotinohydroxamic acid : p_H 9 ; 8 γ Mn/c.c.

C. *iso*Nicotinohydroxamic acid p_H 9 ; 0.2% solution.

D. Nicotinohydroxamic acid : p_H 9 ; 0.2% solution.

Effect of p_H on the Colour Intensity.—With excess of the reagent, optical density was found to increase with increasing p_H up to 9, but thereafter there was no further rise even when a large excess of ammonia was used to make the medium strongly ammoniacal.

Effect of Reagent Concentration on the Colour Intensity.—Variation of the reagent concentration, maintaining the p_H at 9, shows that for maximum colour formation, an amount of the reagent at least fifteen times the molar proportion of manganese is necessary and that a reagent concentration as high as 150 times has no effect on the colour intensity. Generally, for a total of 0.2 mg. Mn, 5 c.c. of 1% reagent solution was used for all the estimations.

Effect of Time on the Colour Intensity.—When the p_H and the reagent concentrations are optimum, the colour takes less than 5 minutes to attain its maximum intensity, otherwise the colour develops slowly.

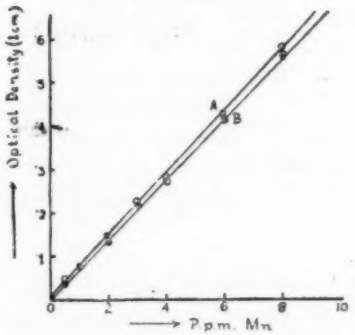
Adherence to Beer's Law.—The coloured product very closely obeys Beer's law over the entire range of investigation, *i.e.*, from 0.25 γ to 10 γ of manganese. However for maximum precision, practical range of measurement should be from 1.5 to 10 γ as the optical density then lies within 0.1 to 0.68.

Stability of Colour.—The colour is perfectly stable at room temperature. A solution having 8γ manganese and excess reagent in presence of excess ammonia gave the same optical density even after a day. The colour intensity remained unchanged within 20-30° over which the readings were taken.

Sensitivity.—The spectrophotometric sensitivity, as calculated from the Beer's law curves, is given by 0.014 γ/cm^2 for nicotino hydroxamic acid and 0.013 γ/ cm^2 for *iso*nicotinohydroxamic acid (Sandell, *loc. cit.*).

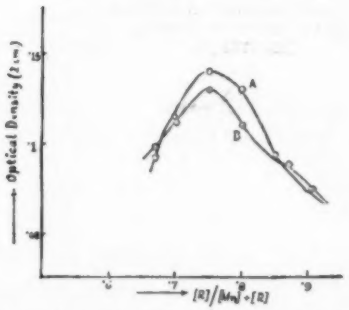
Empirical Composition of the Coloured Product.—This has been determined by following Job's method of continuous variation. However, difficulties were encountered because of the precipitation of manganese in solutions containing smaller amounts of the reagents. Again, since the reagent was not in sufficient excess, the colour was rather slowly developed. Readings were therefore taken after twenty minutes of preparing the solutions. Continuous variation plots with 0.0005 *M* solutions (optical density against mole fraction of reagent) for both the reagents pass through a maximum at a composition of 0.75, indicating the formation of an 1:3 complex between manganese and the hydroxamic acids. As manganic salt of analytically pure grade was not available, experiments by Job's method were carried out with manganous solution (cf. Harvey and Manning, *J. Amer. Chem. Soc.*, 1952, **74**, 4744, for titanium and iron).

FIG. 2
Beer's law curves.



A. Mn-*iso*nicotinohydroxamic acid: p_H 10, 470 mμ.
B. Mn-nicotinohydroxamic acid: p_H 10, 480 mμ.

FIG. 3
Job's curve.



A. Mn-*iso*nicotinohydroxamic acid: p_H 9, 470 mμ.
B. Mn-nicotinohydroxamic acid: p_H 9.0, 480 mμ.

Influence of Foreign Ions on the Colour System.—The effect of various ions has been studied and the approximate tolerance limits determined. A few metallic ions seriously interfere either due to complex formation or due to their reduction. These were, however, masked by suitable complex-formers.

The tolerance limits of different ions have been determined with respect to 4 p.p.m. of Mn in a total volume of 25 c.c. An 1% reagent solution (2.4 c.c.) was used. Ions such as nitrate, sulphate, chloride, acetate, carbonate, tungstate, thiocyanate, iodide and thiosulphate do not interfere even when present in amounts exceeding 1000 p.p.m. The presence of borate, phosphate, tartrate and oxalate can be tolerated up to 1000 p.p.m. although the colour intensity should be measured after 30 minutes of preparing the solution. Cyanide and fluoride should not exceed the limit 200 p.p.m. Cadmium (1000 γ), zinc (500 γ), aluminium (250 γ) and molybdate (1000 γ) do not interfere, if excess ammonia is used to dissolve the precipitates of the metal hydroxides. Hg^{II} (500 γ) does not interfere when masked by excess KI. But Cu, Ni, Co and Ag interfere seriously even when present in small amounts. However Cu

(200 γ), Ni (250 γ), Co (200 γ) and Ag (260 γ) can be tolerated if sodium cyanide solution (1%) is added dropwise to dissolve out the initial precipitates of the metal cyanides and the colour measured after 30 minutes. Ti (60 γ), UO_2^{2+} (80 γ) and VO^{3-} (200 γ) do not interfere when excess ammonia is used and the colour measured at 540-560 mμ. However Fe^{3+} interferes and should therefore be removed before estimating manganese.

The nature and the analytical aspects of the colour reactions of these reagents with vanadium, molybdenum and iron will form the subject matter of future communications.

Author's grateful thanks are due to Prof. P. Rây and to Dr. P. C. Banerjee for their valuable advice and good wishes during the course of this investigations. Thanks are also due to the Government of India, for the award of a senior research scholarship, which enabled him to undertake this work. The author also thanks M/s. Albert David & Co., Calcutta, for a gift of *iso*nicotinic acid.

INORGANIC CHEMISTRY LABORATORY,
INDIAN ASSOCIATION FOR THE
CULTIVATION OF SCIENCE,
CALCUTTA-32.

Received September 7, 1956.

[Jour. Indian Chem. Soc., Vol 34, No 4, 1957]

CHEMISTRY OF BERYLLIUM. PART II. COMPOUNDS OF BERYLLIUM CHLORIDE WITH AMINES

By Sarju Prasad and Kashi Prasad Srivastava

Ammino complexes of $BeCl_2$ with primary, secondary and tertiary amines and diamines have been prepared and their constitution established. Viscometric measurements of β-naphthylamine and o-phenylenediamine in alcohol medium have also been made.

Among the ammoniates of $BeCl_2$, prepared and studied by Ephraim (*Ber.*, 1912, **45**, 1322) and Biltz (*Z. anorg. Chem.*, 1925, **148**, 157), only $BeCl_2.4NH_3$ was found unusually stable towards heat, but it was easily decomposed by water (Sidgwick, "Chemical Elements and their Compounds", Vol. I, p. 208). Though Fricke and co-workers (*Z. anorg. Chem.*, 1924, **146**, 103; 1925, **146**, 121; 1926, **152**, 347, 357; 1927, **163**, 31; 1928, **170**, 25; 1947, **253**, 173) prepared a number of amine complexes (mostly primary amines) with beryllium chloride, but no systematic work was done on this subject.

The present investigation was therefore undertaken with a view to studying the formation of complex compounds of beryllium chloride with primary, secondary and tertiary amines and diamines.

Experimental

Beryllium chloride was prepared by the method of Pollok (*J. Chem. Soc.*, 1904, **85**, 603). Excess of chlorine was removed by passing dry carbon dioxide. A solution of beryllium chloride, dissolved in dry ether, was used in all the experiments. Exact amount of beryllium chloride present in the solution was determined by estimating beryllium and chlorine in a known volume.

To a known volume of beryllium chloride solution, amine solutions in ether of approximately the same strength were added in slight excess with constant stirring. With all the primary and secondary amines the complex formed settled down immediately. In the case of diphenylamine only a slimy precipitate appeared on addition of the amine solution and the complex separated out in fine pink crystals after allowing the mixture to stand overnight in a desiccator ($CaCl_2$). It was washed with dry ether till free of amine (test: filtrate gave no precipitate with $BeCl_2$ solution). The precipitate was pressed between the folds of filter paper and finally dried in vacuum.

In the case of tertiary amines a slight turbidity appeared in the beginning but it disappeared on further addition of amine solutions. The excess of ether was then evaporated on a water-bath and the resulting mixture was allowed to stand in boiling water for 4 hours, cooled and the product washed free of excess of amine with dry ether. The compounds obtained with tertiary amines were very hygroscopic and hence they were quickly transferred to a vacuum desiccator and dried for 2-3 days. These were then analysed in a dry atmosphere.

TABLE I

Amine complexes of $BeCl_2$.

S.No.	Amines	% Beryllium. Found.	Calc.	% Chlorine. Found.	Calc.	% Nitrogen. Found.	Calc.	Colour.	Formula.
1.	*o*-Anisidine	2.70	2.76	21.73	21.78	8.52	8.59	Light grey	$BeCl_2.2CH_3O.C_6H_4NH_2$
2.	*p*-Anisidine	2.74	2.76	21.74	21 78	8.47	8.59	,,	$BeCl_2.2CH_3O.C_6H_4NH_2$
3	*o*-Phenetidine	2.52	2.54	20.02	20.06	7.88	7.91	,,	$BeCl_2.2C_2H_5O.C_6H_4NH_2$
4.	*p*-Phenetidine	2.53	2.54	20 11	20.06	7.88	7.91	,,	$BeCl_2.2C_2H_5O.C_6H_4NH_2$
5.	*m*-toluidine	3.07	3.06	24.10	24.14	9.47	9 50	,,	$BeCl_2.2CH_3.C_6H_4.NH_2$
6.	Benzylamine	3.00	3.06	24.08	24 15	9.53	9 52	White	$BeCl_2.2C_6H_5.CH_2NH_2$
7.	α-Naphthylamine	2.47	2 46	19.42	19.40	7.60	7 65	Light ash	$BeCl_2.2C_{10}H_7.NH_2$
8.	β- ,,	2.48	2.46	19.35	19.40	7.62	7.65	,,	$BeCl_2.2C_{10}H_7.NH_2$
9.	*p*-Phenylenediamine	4.72	4.77	37.77	37.77	14.81	14.89	Dark red	$BeCl_2.C_6H_4(NH_2)_2$
	Do (slight excess)	4 42	4.77	34.80	37.77	...	...	Blue	,, ,, ,,
10.	1:2-Naphthylenediamine	3.78	3.78	29.78	29.79	11.71	11.76	Violet	$BeCl_2.C_{10}H_6(NH_2)_2$
11.	Dianisidine	2 80	2.78	21.96	21 91	8.53	8.64	Ash colour	$BeCl_2[C_6H_3(OCH_3)NH_2]_2$
12.	Ethylaniline	2 79	2.79	22.06	22.05	8.64	8.69	Light yellow	$BeCl_2.2C_6H_5NH.C_2H_5$
13.	Benzylaniline	2.04	2.02	16.19	16.19	6.21	6.29	Grey	$BeCl_2.2(C_6H_5NH.CH_2C_6H_5)$
14.	Diphenylamine	2.69	2.70	21.28	21.29	6.28	6.29	Pink, shining crystals	$2BeCl_2.3(C_6H_5NH\ C_6H_5)$
15.	Dimethylaniline	2 78	2.79	22.04	22.05	8.57	8.69	Green	$BeCl_2.2C_6H_5.N(CH_3)_2$
16.	Diethylaniline	2.42	2.38	18.14	17.78	7.20	7.42	Pink	$BeCl_2.2C_6H_5.N(C_2H_5)_2$
17.	*p*-aminodiethylaniline	2 27	2.26	17.37	17.40	6 87	6.86	Black	$BeCl_2.2C_6H_4N(C_2H_5)_2NH_2$
18.	,, ,, ,,	3 59	3 69	28.38	29.14	...	...	Black	$BeCl_2.C_6H_4.N:C_2H_5)_2NH_2$
19.	Ethylbenzylaniline	1.85	1.79	14 20	14 14	5.51	5 57	Brown	$BeCl_2.2C_6H_5.NCH_2C_6H_5C_2H_5$
20.	Trimethylamine	4.53	4.54	35 85	35.86	14 08	14.14	White	$BeCl_2.2(CH_3)_3N$

Analyses.—A weighed quantity of the substance was decomposed with NaOH solution, the alkali extract neutralised with HCl (dil.) till slightly acidic and beryllium was precipitated as $Be(OH)_2$, which was washed free of electrolytes by 2% ammonium acetate solution. $Be(OH)_2$ was dissolved in dilute HCl and reprecipitated as the hydroxide, washed with 2% ammonium acetate solution, dried, ignited and weighed as BeO.

Chlorine was determined by Piria and Schiff's method and nitrogen by Kjeldahl's method.

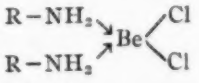
General Properties.—All the complexes are coloured except those obtained with benzylamine and trimethylamine. They do not melt up to 250° but decompose at higher temperatures without melting. Majority of them are insoluble in water and split into $BeCl_2$ and amines such as β-naphthylamine complex, when treated with water, dissociates as :

$$C_{10}H_7NH_2.BeCl_2.C_{10}H_7NH_2 + 6H_2O \rightarrow BeCl_2.4H_2O + \underset{\text{(traces)}}{Be(OH)_2} + 2C_{10}H_7NH_2 + \underset{\text{(traces)}}{C_{10}H_7NH_2.HCl}$$

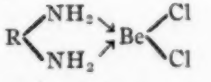
Nearly all the $BeCl_2$ with traces of amine hydrochloride is obtained in the filtrate and amine with traces of $Be(OH)_2$ in the precipitate. These are decomposed by acids and alkalies. They are soluble in alcohol but insoluble in benzene, CCl_4, ether, petroleum ether and acetone, those obtained with *p*-aminodiethylaniline and 1 : 2-naphthylenediamine being sparingly soluble in acetone. Tertiary amine complexes are very hygroscopic ; these and complexes with *o*- and *p*-anisidine, *p*-phenetidine, and ethylaniline are soluble in cold water, while that obtained with *p* aminodiethylaniline is soluble in hot water.

Discussion

Fricke *et al. (loc. cit.)* studied the formation of complex compounds of $BeCl_2$ with several organic compounds and observed that $BeCl_2$ combined with four molecules of ammonia, methylamine and two molecules ethylenediamine, displacing chlorine in the outer ring and with two molecules of methylketone, benzaldehyde, nitrobenzene or other similar compounds when the chlorine remained in the inner ring, forming stable co-ordinate additive compounds. It has, however, been observed that in all the cases studied, two molecules of monoamines and one of diamines attach themselves to one molecule of $BeCl_2$ and can be represented as



in the case of mono-amines, and

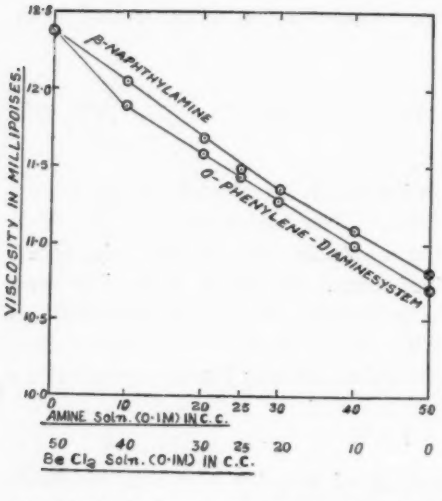


in the case of diamines. These observations show that the molecules attached to the amino group play a predominant part and render the nitrogen atoms sufficiently weak so that they are incapable of displacing chlorine to the outer ring which appears to be due to two reasons : (*i*) steric hindrance of the bigger molecules attached to

$-NH_2$ – NH, and -N- groups and (*ii*) due to weak co-ordinating power of the nitrogen in these amine molecules. The divergence of colours from the original substance and also the deepening of colour in some of the compounds suggest that the complexes formed are of co-valent nature, as has been observed by Pitzer and Hildebrand (*J. Amer. Chem. Soc.*, 1941, **63**, 2475).

An attempt was made to arrive at the constitution of the amine complex by viscometric method but it was not successful. The viscosity was measured in alcoholic medium. Fig. 1 shows that there is a regular decrease in viscosity from $BeCl_2$ to β-naphthylamine and *o*-phenylenediamine as the proportion of amines is increased. From the curves it is evident that the complex formed with $BeCl_2$ and alcohol, $BeCl_2.2EtOH$ (Fricke, *loc. cit.*), is very stable, and hence, the amine or diamine molecule is incapable of displacing the alcohol molecule as it happens in the case of $BeCl_2.2Et_2O$ (Fricke, *loc. cit.*) where the ether molecule is replaced by amine molecules and the complex formed precipitates out.

FIG. 1



That tertiary nitrogen has a weak co-ordinating power is further established by the fact that the tertiary amines form compounds only after heating $BeCl_2$ and amine mixtures on a water-bath for a long time. In the case of *p*-aminodiethylaniline, when the ether solutions were mixed together, an immediate precipitate was formed having the composition $BeCl_2.2A$, but when heated with excess of $BeCl_2$, $BeCl_2.A$ was obtained. The first compound is non-hygroscopic as in the case of compounds having $-NH_2$ group, and the second one is hygroscopic as in the case of compounds having N: group.

p-Phenylenediamine forms a dark red compound having the formula $BeCl_2.C_6H_4(NH_2)_2$, but when a slight excess of amine is added, the colour of the compound abruptly changes to blue and the compound obtained is not hygroscopic as the red compound. The percentages of Be and Cl were found lower than those in the case of the red compound, but no definite formula could be assigned to this compound.

It is interesting to note that diphenylamine affords a compound of the formula $2BeCl_2.3(C_6H_5NH.C_6H_5)$. It seems probable that the secondary nitrogen when directly attached to the bigger molecule offers steric hindrance whereby the octet of only one beryllium atom is complete and other remains incomplete.

The authors' sincere thanks are due to Dr. S. S. Joshi, D.Sc., Head of the Dept. of Chemistry, for providing facilities.

CHEMICAL LABORATORY,
BANARAS HINDU UNIVERSITY,
BANARAS.

Received October 29, 1956.

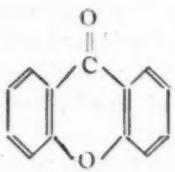
[Jour. Indian Chem. Soc , Vol. 34, No. 4, 1957]

DI-XANTHONES. PART I. CHROMONO-2′ : 3′-2 : 3-XANTHONE

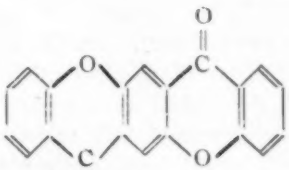
By Tara Singh and S. N. Bedi

2 : 5-Diphenoxyterephthalic acid, prepared by condensing 2 :5-dibromoterephthalic acid with sodium phenoxide, using excess of phenol as a solvent or a diluent, in presence of copper powder, has been cyclised by two different methods to yield chromono-2′ : 3′-2 : 3-xanthone.

Xanthone (I) and its numerous substituted derivatives are known to possess antiseptic and insecticidal properties (Davis and White, *J. Urol.*, 1918, **2**, 107; Fischer, *J. Amer. Chem. Soc.*, 1913, **65**, 991). The γ-pyrone structure is a characteristic feature of the xanthone molecule which might contribute, in part, to its properties.



(I)

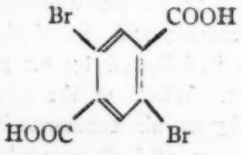


(II)

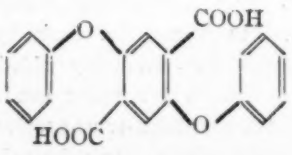
Therefore it was considered worthwhile to prepare organic compounds with two such structural features in the same molecule. Several such compounds are possible. In this communication the preparation of chromono-2′ : 3′-2 : 3-xanthone or the di-xanthone (II) is reported.

2 : 5-Dibromoterephthalic acid (III), required for the preparation of this di-xanthone, was obtained from 2 : 5-dibromo-*p*-xylene according to Marzin (*J. prakt. Chem.*, 1933, **138**, 103). The yield of 2 : 5-dibromo-*p*-toluic acid, reported by Marzin, is not, however, obtainable under the reaction conditions described, but where double the quantity of dilute nitric acid is used and refluxing continued 15 hours, the yield is considerably improved. Some nitration products, insoluble in sodium bicarbonate, have also been found along with 2 : 5 dibromo-*p*-toluic acid.

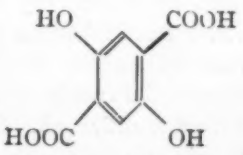
Eckert and Seidal (*ibid.*, 1921, **102**, 338) have reported the preparation of an acid, supposed to be 2 : 5-diphenoxyterephthalic acid (IV), by the condensation of 2 : 5-dibromoterephthalic acid with phenol in the presence of potassium hydroxide and copper powder. This acid (m. p. 314°) is reported to have furnished the di-xanthone (II) when treated with thionyl chloride and anhydrous aluminium chloride. The melting point and the C and H analyses of the di-xanthone have not been reported.



(III)



(IV)



(V)

On repeating the experiments of these workers the present authors could not obtain the 2 : 5-diphenoxyterephthalic acid by this method. The product appeared always to be largely 2 : 5-dihydroxyterephthalic acid (V), as shown by its m.p., equivalent weight and blue fluorescence in alcohol and water (Hemmelmeyer, *Monatsh.*, 1917, **38**, 82; Marzin, *loc. cit.*). This is further supported by our observation that 2 : 5-dibromoterephthalic acid can be easily hydrolysed to 2 : 5-dihydroxyterephthalic acid by boiling with a dilute solution of potassium hydroxide. This product, which is largely 2 : 5-dihydroxyterephthalic acid, is likely to afford an indefinite mixture of substances on treatment with thionyl chloride, followed by anhydrous aluminium chloride.

2 : 5-Diphenoxyterephthalic acid can, however, be easily obtained by the condensation of one molecular proportion of 2 : 5-dibromoterephthalic acid with four of sodium phenoxide in the presence of copper powder and a large excess of phenol acting as a solvent or a diluent. For the conversion of the acid and the phenol into sodium salts, the use of absolute ethyl alcohol is necessary. When lime-distilled alcohol was used, the product was found to be a mixture of 2 : 5-diphenoxyterephthalic acid and 2 : 5-dihydroxyterephthalic acid.

The di-xanthone (II) was easily obtained by treating *pure* 2 : 5-diphenoxyterephthalic acid with phosphorus oxychloride or with phosphorus pentachloride in nitrobenzene, followed by anhydrous aluminium chloride. The impure acid yielded a mixture from which it was difficult to extract the pure di-xanthone.

Experimental

Attempted Condensation of 2 : 5-Dibromoterephthalic Acid with Phenol in the presence of Potassium Hydroxide and Copper Powder.—2 : 5-Dibromoterephthalic acid (0.5 g.), phenol (0.29 g.) and KOH (0.71 g.) were dissolved in 10 c.c. of water. A pinch of copper powder was added and the mixture was refluxed for 3 hours in an oil-bath. Copper powder was filtered off and the filtrate was acidified. The yellow product was crystallised from alcohol in small, yellow needles, m.p. 312° (decomp.). (Found : Equiv., 109.7; calc. for 2 : 5-dihydroxyterephthalic acid, 99; calc. for 2 : 5-diphenoxyterephthalic acid, 175).

In another experiment the same amounts of 2 : 5-dibromoterephthalic acid, phenol and about 0.1 g. copper powder were taken in 10 c.c. of KOH solution (conc.) and refluxed for 3 hours in an oil-bath. The product was worked out as above and it had the same physical constants.

Condensation of 2 : 5-Dibromoterephthalic Acid with Sodium Phenoxide in the presence of Copper Powder and excess of Phenol.—Sodium metal (0.9 g.) was dissolved in absolute alcohol (15 c.c.). 2 : 5-Dibromoterephthalic acid (2 g.) was dissolved in 20 c.c. of freshly distilled phenol in a 100 c.c. flask by warming and the alcoholic solution of sodium ethoxide was then gradually added to it, followed by 0.1 g. of copper powder and the flask was fitted with a water condenser. Whole of the alcohol was then distilled off. The water condenser was replaced by an air condenser fitted with soda-lime guard-tube and the mixture was heated in an oil-bath at 180° for 3 hours. After cooling, enough ether was added to dissolve out the excess of phenol

and the solution was filtered. The residue was washed with fresh ether till the phenol was completely removed. It was dissolved in water, filtered to remove the copper and the filtrate was acidified. The precipitated substance was filtered, treated with sodium bicarbonate (charcoal), filtered again and decomposed with HCl (dil.), yield 1.4 g. It was twice crystallised from glacial acetic acid to afford a crystalline powder, m.p. 267°. (Found: Equiv, 173, 178. C, 67.65; H, 4.2. $C_{20}H_{14}O_6$ requires equiv., 175; C, 68.28; H, 4.0%).

The Di-xanthone.—(*a*). 2:5-Diphenoxyterephthalic acid (pure, m.p. 267°) (0.23 g.) was mixed with $POCl_3$ (5 c.c.) and the mixture heated in an oil-bath. A brisk reaction started with the evolution of HCl gas at 95°. The reaction mixture was refluxed for one hour, keeping the bath temperature at 120-25°. $POCl_3$ was then distilled off under reduced pressure and the residue treated with powdered ice and made alkaline with dilute NaOH solution. The insolubie precipitate was filtered, washed free of alkali and dried; yield 0.14 g. It was crystallised from toluene in small, yellow needles, m.p. 404° (aluminium block) with sublimation and slight decomposition. (Found: C, 76.25; H, 3.02. $C_{20}H_{10}O_4$ requires C, 76.4; H, 3.18%).

(*b*). The pure 2:5-diphenoxyterephthalic acid (0.1 g.) was dissolved in 3 c.c. of freshly distilled nitrobenzene on warming in a 10 c.c. Erlenmeyer flask. To this was added PCl_5 (0.45 g.), followed by $AlCl_3$ (anhyd., 0.2 g.). The mixture was heated on a water-bath for half an hour till the evolution of HCl gas had stopped. Nitrobenzene was removed under reduced pressure and the remaining red residue was treated with ice. The mixture was made alkaline with NaOH solution, filtered and washed free of alkali. The dried product weighed 80 mg. It was crystallised from toluene in yellow crystalline powder, m.p. 404°.

Department of Chemistry,
Government College,
Ludhiana, Panjab.

Received June 6, 1956.

INTERACTION OF AROMATIC HYDROXY KETONES AND THEIR DERIVATIVES AND THIONYL CHLORIDE IN PRESENCE OF FINELY DIVIDED COPPER. PART XII. PREPARATION OF 2 : 2′-DIHYDROXY-3 : 3′-DIACETYL-4 : 4′-DIMETHOXY-DIPHENYL THIOETHER AND DERIVATIVES

By V. J. Dalvi and G. V. Jadhav

2 : 2′-Dihydroxy-3 : 3′-diacetyl-4 : 4′-dimethoxydiphenyl thioether and its diacetyl, dimethyl and 2 : 4-dinitrophenylhydrazone derivatives have been prepared. Its constitution has been established by nitration and bromination.

During investigation in this line of work (*vide* this *Journal*, 1956, **33**, 807) it was observed that the ketonic group in the γ-position in resorcinol greatly activated the molecule, as no definite product could be isolated even though the reaction with thionyl chloride in the presence of copper was carried out at a very low temperature in the case of 2-acetylresorcinol. When, however, the reaction was carried out with the monomethyl ether of 2-acetylresorcinol, the thioether (I) was obtained. Its constitution has been established by nitration, yielding 2-hydroxy-3-nitro-6-methoxyacetophenone (III), proved by mixed melting point with the genuine specimen of the compound prepared by the method of Naik, Thakore and Shah (*Proc. Ind. Acad. Sci.*, 1953, **37A**, 765). The diacetyl, dimethyl and 2 : 4-dinitrophenylhydrazone derivatives of (I) have also been prepared.

Action of bromine in acetic acid medium on the thioether (I) furnished the dibromo thioether (II) which with nitric acid afforded a bromo-nitro derivative, free from sulphur, and identical with the bromo derivative obtained from (III) by the action of bromine. It has been assigned the constitution 2-hydroxy-3-nitro-5-bromo-6-methoxy-acetophenone, based on rules of substitution. (II) is therefore 5 : 5′-dibromo derivative of (I).

Bromine in acetic acid medium at a higher temperature afforded a tetrabromo derivative without sulphur in it, and which lost two bromine atoms on boiling with aqueous potassium hydroxide.

Experimental

2 : 2′-Dihydroxy-3 : 3′-diacetyl-4 : 4′-dimethoxydiphenyl Thioether (I).—Finely divided copper (6 g.) was gradually added to the solution of thionyl chloride (9 c. c.) in dry chloroform (60 c. c.), cooled in an ice bath. After about half an hour, 2-hydroxy-6-methoxy acetophenone (10 g.) was added to it at room temperature and the mixture was left overnight. It was filtered and the residue washed with dry chloroform. After removal of chloroform (at room temperature) a yellow paste remained behind. It was first treated with petroleum ether (b.p. 40°-60°) and the residue was then treated with acetic acid, when a yellow powder separated out. It was crystallised from alcohol in pale yellow shining needles, m. p. 184-85°, yield, 2.5 g. (Found : C, 59.92; H, 5.0 ; S, 9.08. $C_{18}H_{18}O_6S$ requires C, 59.68 ; H, 4.97 ; S, 8.84 %).

It is soluble in dilute NaOH solution. It shows a bottle green coloration with EtOH-$FeCl_3$.

The same thioether was also formed when the solution of the ketone (3 g.) in dry ether (50 c. c.), cooled in ice, was treated with sulphur monochloride or sulphur dichloride (1.5 g.) and the reaction was allowed to proceed at that temperature for 1 hour and then the mixture was left overnight at room temperature. The paste obtained after removal of the ether from the filtrate was worked up as above, yield 0.6 g.

Diacetyl derivative (I) was prepared by heating on a boiling water-bath for half an hour the solution of the thioether (0.5 g.) in acetic anhydride (5 c. c.) in presence of a drop of H_2SO_4 (conc.). It crystallised from a mixture of benzene and petroleum ether (40°-60°) in colorless plates, m. p. 106-107°. (Found : S, 7.24. $C_{22}H_{22}O_8S$ requires S, 7.17 %).

It did not show any colour with alcoholic EtOH-$FeCl_3$ nor dissolved in NaOH solution.

Dimethyl ether of the thioether (I) was prepared by refluxing on the water-bath the solution of the thioether (I : 0.5 g.) in dry acetone (25 c.c.) with dimethyl sulphate (0.5 c. c.) in presence of anhydrous potassium carbonate (1 g.). The solid obtained from the filtrate was crystallised from alcohol in colorless needles, m. p. 135-36°. (Found : S, 8.07. $C_{26}H_{22}O_6S$ requires S, 8.2 %).

It did not develop any colour with E_tOH-$FeCl_3$ nor dissolve in NaOH solution.

2 : 4-*Dinitrophenylhydrazone of* (I) was obtained as orange needles, m. p. 230-31°. (Found : N, 15.56 ; S, 4.2. $C_{30}H_{26}O_{12}N_8S$ requires N, 15.52 ; S, 4.43 %).

2-*Hydroxy-3-nitro-6-methoxyacetophenone* (III).—The thioether (I: 1 g.) was gradually added to nitric acid (*d* 1.4, 10 c.c.), cooled in ice. The reaction was then allowed to proceed at that temperature for about 10 minutes and the mixture was poured over crushed ice. The yellow solid obtained was crystallised from dilute alcohol in cream-coloured needles, m. p. 102-103°. (Found : N, 6.5. Calc. for $C_9H_9O_5N$: N, 6.63 %). Mixed m. p. with the genuine specimen showed no lowering in m. p. (Naik, Thakore and Shah, *loc. cit.*).

The *thioether* (II) was formed when acetic acid solution of bromine (5 c. c. of 20 % w/v) was added to the hot solution of the thioether (I : 1 g.) in acetic acid (20 c.c.) and the reaction mixture was left overnight at room temperature. The solid obtained on dilution was crystallised from dilute acetic acid in yellow needles, m. p. 199-200°. (Found : Br, 30.59 ; S, 6.25. $C_{18}H_{16}O_6Br_2S$ requires Br, 30.77 ; S, 6.15 %).

2-*Hydroxy-3-nitro-5-bromo-6-methoxyacetophenone*.—The solution of the thioether (II : 0.5 g.) in acetic acid (5 c. c.) was cooled in ice and nitric acid (*d* 1.4, 5 c.c.) was added to it at that temperature. The reaction was allowed to proceed at that temperature for about 10 minutes and then the mixture was poured over crushed ice when a yellow solid was obtained. This was crystallised from acetic acid, m.p. 156-57°. (Found : N, 4.7 ; Br, 27.43. Calc. for $C_9H_8O_5NBr$: N, 4.83 ; Br, 27.58 %). Mixed m. p. with the monobromo derivative obtained by the action of acetic acid solution of bromine (4 c.c. of 20% w/v) on the solution of 2-hydroxy-3-nitro 6-methoxyacetophenone (III: 1 g.) in acetic acid (5 c. c.) at room temperature showed no depression.

2-Hydroxy-6-methoxytetrabromoacetophenone was formed when the solution of bromine (2 c.c.) in acetic acid (10 c.c.) was added to the solution of the thioether (I : 1 g.) in acetic acid (20 c. c.), and the mixture heated on a boiling water-bath for 4 hours. The solid obtained on dilution of the reaction mixture was crystallised from dilute alcohol in lemon-yellow needles, m. p. 101-102°. (Found : Br, 66.18. $C_9H_6O_3Br_4$ requires Br, 66.39 %). A known weight of the tetra bromoderivative was boiled for 2 hours with a 20% KOH solution (excess) and then acidified with nitric acid, and bromine in aqueous solution was estimated. (Found : Br, 33.9. Calc for 2 Br in $C_9H_6O_3Br_4$: Br, 33.2 %).

THE ORGANIC CHEMISTRY LABORATORY,
THE INSTITUTE OF SCIENCE, BOMBAY.

Received March 6, 1956

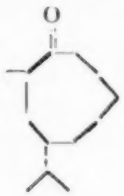
[Jour. Indian Chem. Soc., Vol. 34, No. 4, 1957]

MONOTERPENOIDS. PART II. SYNTHESIS OF 2-METHYL-5-*iso*PROPYL-SUBERONE AND 3-METHYL-6-*iso*PROPYLSUBERONE

By T. M. Jacob and Sukh Dev

Synthesis of 2-methyl-5-*iso*propylsuberone and 3-methyl-6-*iso*propylsuberone, starting from tetrahydrocarvone, has been achieved and their light absorption and other properties have been studied with a view to finding out a method for their estimation in a mixture.

In connection with the projected syntheses in the guaiazulene series, 2-methyl-5-*iso*propylsuberone (I) appeared to be a suitable starting material. It was planned to study the ring-expansion of carvomenthone (II) in this connection. Since the ring-enlargement of tetrahydrocarvone (II) could possibly proceed in either direction to furnish 2-methyl-5-*iso*propylsuberone (I) or 3-methyl-6-*iso*propylsuberone (III), it became necessary to have authentic data about the properties of (I) and (III). This communication describes the synthesis of these hitherto-unknown ketones.

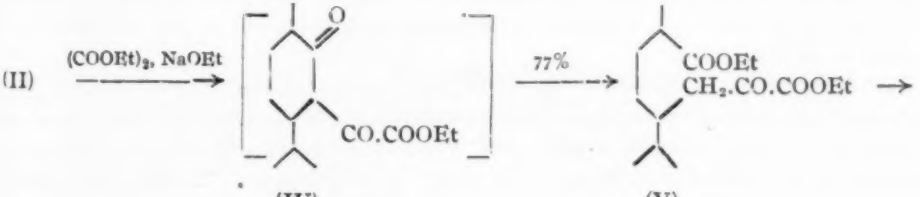


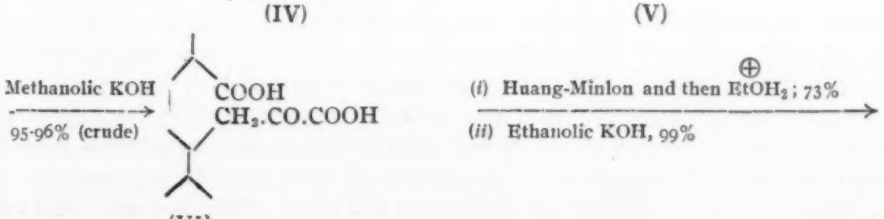
(I)

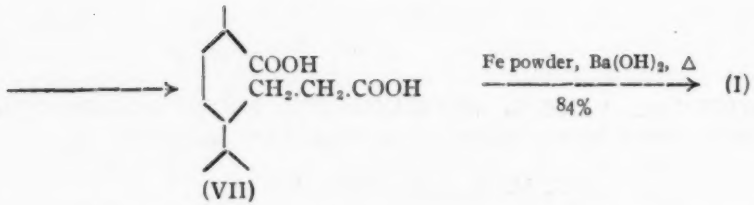
(II)

(III)

*2-Methyl-5-iso**propylsuberone* (I).— The method used for the synthesis of (I) is schematically represented below. The synthesis utilises 1-methyl-4-*iso*propyl-6-oxo-suberic acid (VI) of Bradfield, Jones and Simonsen (*J. Chem. Soc.*, 1935, 315).

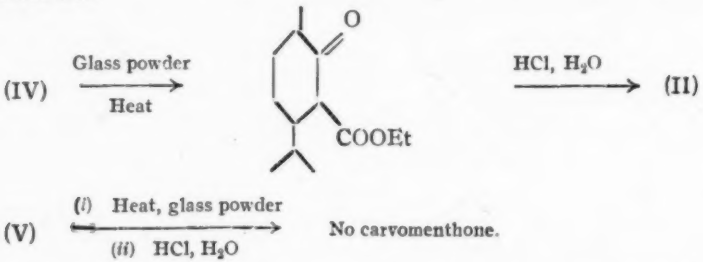






(VII)

These authors in an effort to prepare the glyoxylate (IV) carried out the condensation of tetrahydrocarvone and diethyl oxalate according to the general method of Kotz and co-workers (*J. prakt. Chem.*, 1913, **88**, 261 ; *Annalen*, 1906, **350**, 217 ; 1907, **357**, 192). However, the only product isolated proved to be the cleavage material (V). Since this reaction constitutes the starting point for the present synthesis, it has been studied in some details. The authors treated the distilled condensation product with methyl alcoholic potash to hydrolyse the ester, and the acid, thus obtained, was proved to be (VI). In order to find out the stage at which this base-catalysed cleavage must have occurred (*i.e.* during condensation or alkaline hydrolysis), the following reaction was carried out.



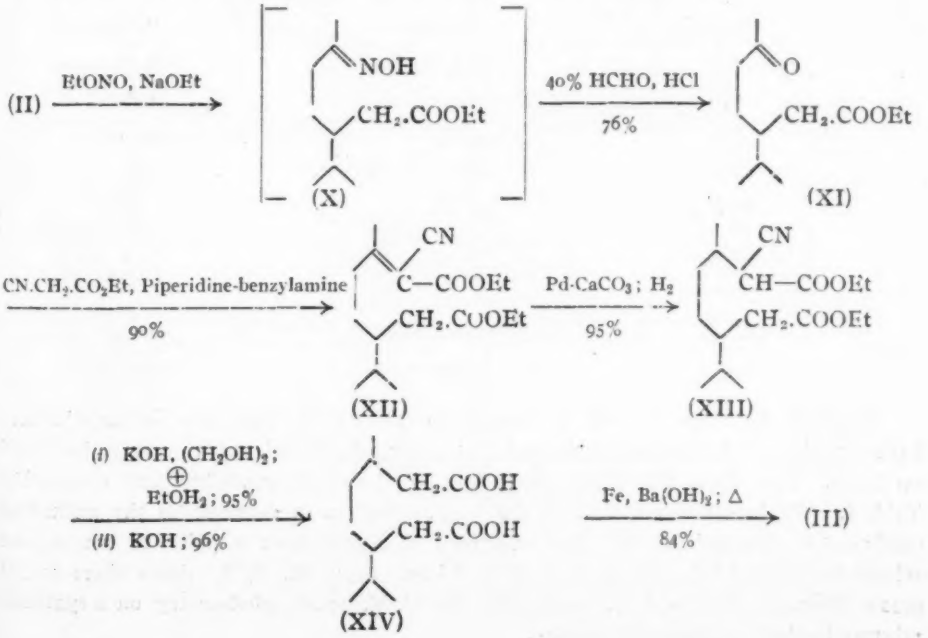
The condensation product was heated with glass powder (Bachmann *et al.*, *J. Amer. Chem. Soc.*, 1940, **62**, 831) and the distilled material was hydrolysed with acid. Since practically no carvomenthone could be isolated, it was evident that the fission had occurred during condensation. By slightly modifying the conditions for the condensation, somewhat improved yields (77% instead of 64% reported) of the product (V) could be obtained.

The cleavage product (V) was hydrolysed with alkali and the crude acid (VI) obtained was reduced by the Huang-Minlon modification of the Wolff-Kishner reduction to provide 1-methyl-4-*iso*propylsuberic acid (VII). The reduced acid (VII) was best purified by rectification of its ethyl ester, followed by its hydrolysis. There are not many recorded instances of the reduction of α-keto-acids (Mosbach *et al.*, *J. Amer Chem. Soc.*, 1951, **73**, 5477). A study of the optimum conditions for this reduction showed that five moles of 60% hydrazine hydrate for each mole of the keto-acid (VI) gave fairly good yields of the required product. Since this method of preparation of (VII) utilises ethyl oxalate to add on a chain of two carbon atoms, it was thought worthwhile to see if the alkaline Wolff-Kishner reduction (cf. Stetter *et al.*, *Ber.*, 1954, **87**, 869, 990, 1617) of *cyclo*hexanone-2-glyoxylate could furnish suberic acid itself. This, however, could not be achieved.

For the conversion of 1-methyl 4-*iso*propylsuberic acid (VII) to 2-methyl-5-*iso*propylsuberone (I), the dry-distillation method was employed. Of the various modifications (D.R.P., 256,622 ; Aschan, *Ber.*, 1912, **45**, 1603 ; Ruzicka *et al.*, *Helv. Chim. Acta*, 1926, **9**, 249, 399, 499 ; 1928, **11**, 496, 670, 686 ; Stoll and Rouve, *ibid.*, 1944, **27**, 1570 ; Vogel, *J. Chem. Soc.*, 1928, 2032) of this reaction, the one utilising the various salts (Ruzicka *et al.*, *loc. cit.* ; Stoll and Rouve, *loc. cit.*) (especially those of rare earths) has been well investigated. A literature survey showed that the simpler method of Vogel (*loc. cit.*) utilising $Ba(OH)_2.8H_2O$ and iron powder afforded superior yields of suberones than the one employing rare earth salts for dry distillation (cf. Sörm and Fajkos, *Coll. Czech. Chem. Comm.*, 1947, **12**, 81 ; Plattner and Studer, *Helv. Chim. Acta*, 1946, **29**, 1432 ; Pommer, *Annalen*, 1953, **579**, 65). Vogel's method, which has been extensively employed by Sörm *et al.* (*Coll. Czech. Chem. Comm.*, 1947, **12**, 251, 554 ; 1949, **14**, 345 , 1951, **16**, 168, 184 ; 1955, **20**, 227) in the azulene chemistry, was used for the preparation of (I) when consistent yields of 80-85% could be obtained.

The properties of this ketone are recorded in Table I and its spectral properties have been discussed later.

*3-Methyl-6-iso*propylsuberone (III).—This ketone has been synthesised by following the route outlined below. The keto-ester (XI) and its acid have been described in the literature. The keto-acid has been obtained by the oxidation of carvomenthone with potassium permanganate (Baeyer, *Ber.*, 1896, **29**, 36), chromic acid (Wallach, *Annalen*, 1905, **339**, 113), pervanadic acid (Triebs, *Ber.*, 1939, **72**, 1199), and by its cleavage with amyl nitrite-HCl (Baeyer, *ibid.*, 1896, **29**, 31).



All these procedures furnish the keto-acid in a poor yield. By the application of the base-catalysed ethyl nitrite-ketone fission reaction (Clarke *et al.*, *J. Chem. Soc.*, 1908, **93**, 30 ; Woodward and Doering, *J. Amer. Chem. Soc.*, 1945, **67**, 866 ; Touster, "Organic Reactions", John Wiley, New York, 1953, Vol. VII, p. 327) to carvomenthone (II), it has been possible to prepare the keto-ester in a yield of 76%. The intermediate oximino-ester (X) was directly converted into (XI) by a short treatment with formalin and hydrochloric acid (Barltrop *et al.*, *J. Chem. Soc.*, 1951, 181 ; Koelsch and Le Claire, *J. Org. Chem.*, 1941, **6**, 516).

The keto-ester on treatment with ethyl cyanoacetate in the presence of piperidine containing benzylamine (Sukh Dev, this *Journal*, 1953, **30**, 665) readily furnished the desired condensation product (XII), which on catalytic reduction over palladium-on-calcium carbonate (Busch, *Ber.*, 1916, **49**, 1063 ; 1929, **62**, 1458) yielded the diethyl 1-cyano-2-methyl-5-*iso*propylsuberate (XIII).

Acid-hydrolysis of (XIII) was slow and incomplete. However, on treatment with potassium hydroxide in ethyleneglycol, both hydrolysis and decarboxylation took place to furnish practically a quantitative yield of the suberic acid (XIV) ; this was also best purified through its diethyl ester. The dicarboxylic acid (XIV) was converted in a yield of 84% to the corresponding 3-methyl-6-*iso*propylsuberone (III). The properties of this ketone are recorded in Table I.

The ketones (I) and (III) can both occur as *cis*- and *trans*-stereoisomers, but at present no assignment of configuration is possible.

TABLE I

Properties.	Ketone (I).	Ketone (III)
B.P.	86-87°/2.5 mm	87°/2.5 mm
η_D^{28}	1.4620	1.4610
d_4^{28}	0.9105	0.9076
M_D	50.75 [calc. M_D 50.81]	50 81
$[\alpha]_D^{28}$	+ 6°.81	− 2° 5
	(*c*, 2 205% in ethanol)	(*c*, 1.583% in ethanol)
λ_{max}^{EtOH}	280 mμ (ε 37)	283 mμ (ε 26)
$\lambda_{max}^{n\text{-heptane}}$	285 mμ (ε 23)	292 mμ (ε 21)
Odour	Deodar wood	Peppermint

Spectral characteristics.—It is clear from Table I that these two isomeric ketones have very similar physical properties and that a method of estimation cannot be based on them. The ultraviolet light absorption for these compounds has been recorded in Table I. The bathochromic shift for the λ_{max} as well as a decrease in the extinction coefficient ε observed for the two suberones in going from a polar to a non-polar solvent is expected (Mariella *et al.*, *J. Org. Chem.* 1954, **19**, 678). Since there is not much difference in the λ_{max}, estimation by U. V. spectrophotometry on a synthetic mixture in alcohol gave erratic results.

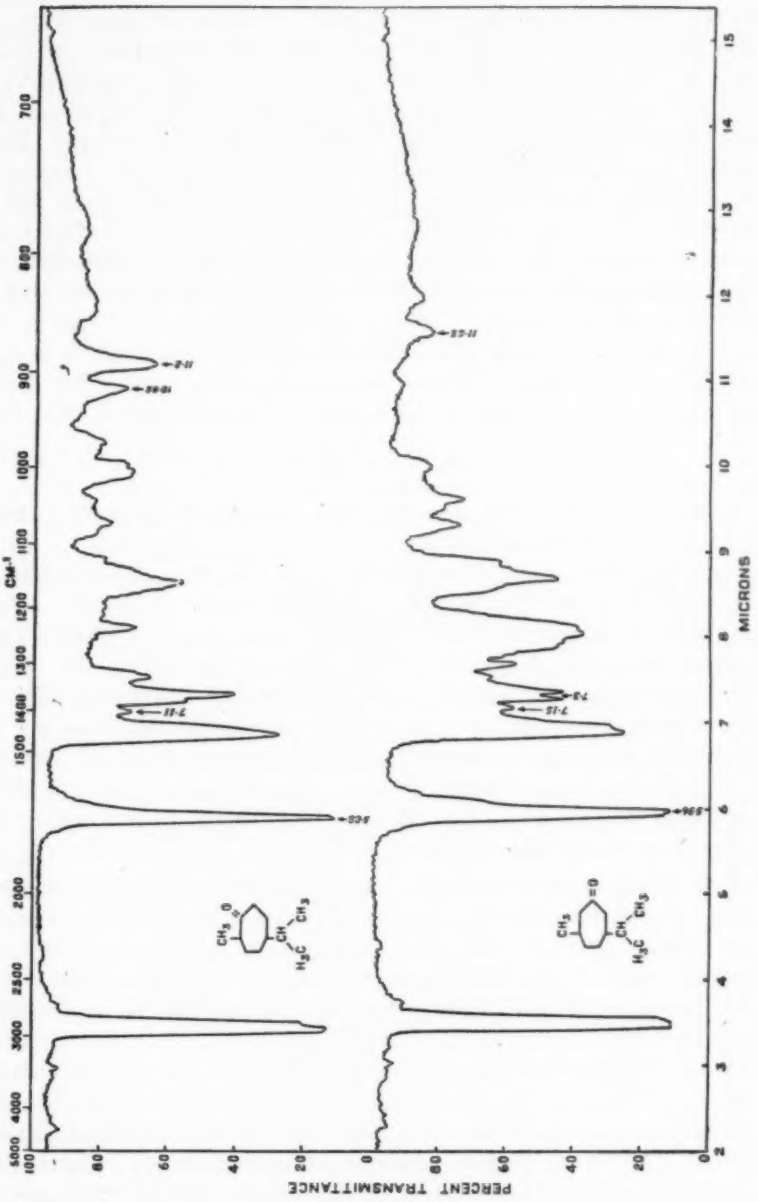


FIG 1

The infra red spectra for the two ketones (I) and (III) are shown in Fig. 1. As expected the C═══O stretching vibration occurs at 5.88μ for the ketone (I) and at 5.96μ for the second isomer; it has been established (Rasmussen in Zechmeister's "Progress in the Chemistry of Organic Natural Products", Springer-Verlag, 1948, p. 331) that the C═══O frequency is dependent on ring-strain and that suberones* absorb more at lower frequency than the 6-membered ketones. The bands at 7.11μ and 7.15μ for the ketones (I) and (III) respectively are to be ascribed to the scissoring frequency of the methylene group next to the carbonyl (Jones and Sandorfy in Weissberger's "Technique of Organic Chemistry", Interscience Publishers Inc., New York, 1956, Vol. IX, p. 498). Whereas the ketone (II) shows a well-defined doublet at 7.3μ, characteristic of the gem-dimethyl (Bellamy, "The Infra-red Spectra of Complex Molecules", John Wiley, New York, 1954, p. 23), it is not so well defined in the isomer (I). In the fingerprint region, (I) exhibits two characteristic bands at 10.92μ and 11.2μ, which are not present in (II), and consequently can be utilised for its estimation; similarly ketone (II) has a band at 11.56μ useful for its determination.

EXPERIMENTAL

Melting and boiling points are uncorrected. The ultraviolet spectra were measured on a Beckman DU spectrophotometer.

Tetrahydrocarvone (II).—The carvone used in these experiments had b. p. 150-52°/50 mm, 126-27°/34 mm, η_D^{25} 1.4970, $[\alpha]_D^{25}$ + 57°.2.

A mixture of freshly distilled carvone (37.5 g., 0.25 *M*), ethanol (distilled over Raney nickel) and Pd-$CaCO_3$ catalyst (6 g.) was hydrogenated in the usual manner. The solvent was removed and the residue fractionated through an efficient column. The desired product was collected at 115-16°/30 mm; the η_D^{25} varied as the distillation proceeded from 1.4535 to 1.4538 and the $[\alpha]_D^{25}$ changed from -31°.4 to -26°; yield 64-66%. A higher boiling fraction with b.p. 117-34°/30 mm, η_D^{25} 1.4925 and $[\alpha]_D^{25}$ -12° amounted to about 30% (Read and Johnston, *J. Chem. Soc.*, 1934, 226, record for tetrahydrocarvone: b.p. 98-99°/16 mm, η_D^{20} 1.4552, $[\alpha]_D$ -30° 37′).

1-*Methyl*-4-iso*propyl*-6-*oxosuberic Acid* (VI).—To an ice-cooled solution of sodium (16.1 g., 0.7 g. atom) in absolute ethanol (200 c.c.) a well-cooled mixture of carvomenthone (90 g., 0.584*M*) and ethyl oxalate (108 g., 0.74*M*) was added during a few minutes with swirling. The light orange mixture was allowed to stand at 0°-5° for 36 hours and then at room temperature (25°) for another 12 hours. The reddish solution was then poured on ice (500 g.) and H_2SO_4 (C.P., 30 c.c.) covered with ether (150 c.c.). The solvent layer was separated and the aqueous phase extracted with ether (50 c.c. × 2). The combined extracts were washed with aqueous sodium bicarbonate (50 c.c. × 2) and then with brine (50 c.c. × 2) and dried (Na_2SO_4). The solvent was distilled off (column) and the residue fractionated. The required product (V) distilled at b.p. 152-55°/1.5 mm; η_D^{24} 1.4610–1.4595, yield 75-77% (131-135 g.).

* Suberone has been stated to exhibit its C = O band at 1699 cm^{-1} (Scott and Tarbell, *J. Amer. Chem. Soc.*, 1950, **72**, 240).

{ 1703 (liquid) (Sörm, *et al.*, *Coll. Czech. Chem. Comm.*, 1950, **15**, 186).
{ 1694 (solution).

The above product (81.1 g.) was refluxed with methanolic KOH (60 g. of KOH in 50 c.c. water and 600 c.c. MeOH) for 3 hours. This was filtered to remove a small precipitate and then most of the alcohol was distilled off. The residue was diluted with water (100 c.c.) and extracted with ether to remove any neutral material. The alkaline portion was acidified with HCl (dil.), saturated with sodium chloride and extracted with ether (75 c.c. × 4). The combined extract was washed once with brine and dried (Na_2SO_4). Removal of the solvent left the crude acid (VI) as a gum ; yield 63.3 g. (96%). This was used as such in the next step.

In order to determine the stage at which cleavage had occurred, the keto-ester (V : 5.8 g.) was heated with glass powder (3 g.) at 160-70° for 2 hours and worked up with ether. The product was distilled in vacuum : b.p. 164°/3 mm, $\eta_D^{28\cdot5}$ 1.4495, yield 4.15 g. This material was refluxed with HCl (C.P., 25 c.c.) and water (10 c.c.) for 10 hours and treated with sodium bicarbonate to separate acidic and neutral portions ; the latter was negligible.

1-*Methyl*-4-iso*propylsuberic Acid* (VII).—To a solution of KOH (60 g.) in ethyleneglycol (300 c.c.) the above keto-acid (36.5 g., 0.15 *M*) and hydrazine hydrate (60%, 62.5 c.c., 0.75 *M*) were added. After refluxing for 3½ hours, the excess of hydrazine hydrate and water were allowed to escape during 2 hours till the contents registered a temperature of 190-95°. The product was again refluxed for another 6 hours, cooled, diluted with water (100 c.c.), acidified with HCl and extracted with ether (50 c.c. × 4) after salting with brine. From the combined extracts, solvent was flashed off and the residue was diluted with benzene (40 c.c.), which was distilled off. The crude acid (VII), thus obtained, was esterified by heating it with benzene (40 c. c.), alcohol (25 c. c.) and H_2SO_4 (conc., 0.5 c. c.) through azeotropic distillation. The separation of water ceased after one hour, but the heating was continued for another hour. The product was cooled and washed with water (20 c. c. × 2). The aqueous portion was extracted with benzene (20 c.c.) and the combined benzene solutions washed once with brine containing sodium carbonate, and dried (Na_2SO_4). The solvent was removed (column) and the crude ester fractionated to afford the *diethyl* 1-*methyl*-4-iso*propylsuberate* as a colorless liquid : b.p. 141°/2 mm, $\eta_D^{28\cdot5}$ 1.4410, yield 31 g. (73%). An analytical sample had b.p. 135°/1.5 mm, η_D^{27} 1 4390, d_4^{27} 0.9504, M_D 79.12 (calc. 79.42), M.W. by saponification, 290.4 (calc. 286). (Found : C, 67.22 ; H, 10.76. $C_{16}H_{30}O_4$ requires C, 67.13 ; H, 10.49%).

The pure ester (85.5 g., 0.3 *M*) was saponified with ethanolic KOH (50 g. KOH, 50 c.c. water, 450 c.c. of alcohol) by gently refluxing for 12 hours. The alcohol was distilled off, the residue cooled, diluted with water (200 c.c.), washed once with ether and acidified with HCl (Congo red). After saturation with sodium chloride, the acid was taken up in ether (150 c.c. × 3) washed with brine and dried (Na_2SO_4). Removal of the solvent left the acid (68.4 g., 99.5%) as a thick liquid, which failed to solidify. An analytical sample was prepared by short-path distillation from a 'rocket' (bath temperature 130°/0.05 mm). (Found : C, 62.69 ; H, 9.74. $C_{12}H_{22}O_4$ requires C, 62.62 ; H, 9.56%).

2-Methyl-5-isopropylcycloheptanone (I).—Iron powder (Merck) was heated in a current of pure, dry hydrogen at 450° for 4 hours and then allowed to cool in an atmosphere of hydrogen. The preparation was used up within a month.

The dibasic acid (VII: 16.3 g.) was thoroughly mixed with the above iron powder (16.3 g.) and finely powdered crystalline barium hydroxide (1 g.) in a distillation flask (125 c.c.). The neck of the flask was fitted with a thermometer dipping into the mixture and the whole was assembled for distillation. The mixture was heated manually with a free flame. A lot of fumes evolved in the beginning, followed by a few drops of water. The ketone started distilling at 280°, but the contents were heated strongly so that the inside temperature was 300°-360°. After the pyrolysis was over (½ hour), the flask was cooled and then water (30 c.c.) was added which was distilled off to co-distil any residual ketone. The product was taken up in ether (20 c.c. × 3), washed with brine and dried (Na_2SO_4). The solvent was carefully removed (column) and the residue distilled to give a colorless liquid with an intense odour of "deodar" wood, b.p. 74°/1 mm, yield 10 g. (84%). The properties of the analytical sample have been recorded in Table I. (Found: C, 78.51; H, 11.91. $C_{11}H_{20}O$ requires C, 78.57; H, 11.91%).

The *semicarbazone* (pyridine method) after three crystallisations from dilute alcohol was obtained as white lustrous leaflets, m.p. 150-51°. (Found: N, 18.58. $C_{12}H_{23}ON_3$ requires N, 18.66%).

The *2:4-dinitrophenylhydrazone* (H_2SO_4 method) after three crystallisations from alcohol furnished lustrous yellow plates, m.p. 115.5-16°. (Found: N, 16.54. $C_{17}H_{24}O_4N_4$ requires N, 16.09%).

Ethyl 2-isoPropyl-5-oxo-n-heptanoate (XI).—Ethyl nitrite was dried over solid KOH and was distilled from it immediately before use.

To well-cooled carvomenthone (32.8 g., 0.213*M*), contained in a litre flask protected from moisture, an ice-cold solution of sodium (4.9 g., 0.213 g. atom) in alcohol (100c.c.) was added. This was diluted with absolute alcohol (500 c.c.) and then thoroughly chilled. Ethyl nitrite (27 g., 0.36 *M*) was added in one lot with swirling and cooling. The reaction mixture was allowed to stand at 0°-5° for 18 hours. Through the reddish orange solution, thus obtained, dry carbon dioxide was bubbled for about 3 hours, warmed and the precipitated sodium carbonate filtered off. The alcohol was removed (column) from a steam-bath to afford the crude oximino ester. To this formaldehyde (40%; 25 c.c.) and HCl (2*N*, 7.8 c.c.) were added and the mixture warmed on a steam-bath for 10 minutes with swirling, when the top layer became dark. This was cooled and the product extracted with ether (25 c.c. × 5) and the combined extracts washed with sodium carbonate solution (20 c.c. × 2) and then with brine (20 c.c. × 2) and dried (Na_2SO_4). The material was stripped off the solvent and the residue fractionated to give after a small fore-run (1.75 g.) the desired keto-ester (XI) as a colorless liquid: b.p. 123-26°/6mm, η_D^{27} 1.4385, yield 30.7 g. (75.8%). (Baeyer, (*loc. cit.*) records b.p. 143-46°/12 mm.

An analytical sample (refractionated: central cut) had b. p. 116-18°/3.5 mm, η_D^{26} 1.4380, d_4^{26} 0.9543, M_D 58.84 (calc. 59.3), $[\alpha]_D^{30}$ -1°.2.

Diethyl 1-Cyano-2-methyl-5-isopropyl-Δ^1-suberate (XII).—A mixture of the keto-ester (XI: 36.95 g., 0.173 *M*), ethyl cyanoacetate (22.6 g., 0.2 *M*), piperidine (1.53 g., 0.018 *M*), benzylamine (0.214 g.), glacial acetic acid (6 c.c.) and benzene (100 c.c.) was refluxed with the continuous removal of water. Separation of water ceased after one hour. After heating for another ½ an hour, the product was cooled, diluted with ether (200 c.c.) and washed successively with water (30 c.c. × 2) and brine (50 c.c. × 1). After drying (Na_2SO_4) the solvent was removed and the residue fractionated (Vigreux column). The condensation product was obtained as a colorless liquid: b.p. 175–75°/2 mm, η_D^{32} 1.4695, yield 47.3 g. (88.6%).

A sample was refractionated for analysis: b.p. 169-73°/2 mm, η_D^{25} 1.4700, d_4^{25} 1.016, M_D 84.89 (calc. 83.3, EM_D 1.59, $E\sum_D$ 0.51), $[\alpha]_D^{25}$ -10°.2. (Found: C, 66.15; H, 8.76; N, 4.6. $C_{17}H_{27}O_4N$ requires C, 66.01; H, 8.74; N, 4.53%).

Diethyl 1-Cyano-2-methyl-5-isopropylsuberate (XIII).—The above unsaturated ester (49.9 g., 0.161 *M*) in ethanol (distilled over Raney nickel, 200 c.c.) was hydrogenated over Pd-$CaCO_3$ catalyst (5 g.) at room temperature and pressure. The reduction came to a close after a take-up of 101% of the theoretical amount of hydrogen during 16-20 hours. After processing in the usual way the product was fractionated to yield a colorless liquid: b.p. 169°/2 mm, η_D^{25} 1.4480, yield 47.4 g. (94.4%).

A purified sample had b.p. 169°/2 mm, η_D^{25} 1.4480, d_4^{25} 0.9974, M_D 83.51 (calc. 83.79), $[\alpha]_D^{25}$ -3°.2. (Found: C, 65.0; H, 9.29; N, 4.29. $C_{17}H_{29}O_4N$ requires C, 65.53; H, 9.32; N, 4.5%).

Diethyl 2-Methyl-5-isopropylsuberate.—The reduced cyano-ester (XIII: 13.9 g.) was refluxed with KOH (10 g. in 10 c.c. of water) in ethyleneglycol (60 c.c.) till the evolution of ammonia had ceased (7-10 hours). The cooled material was diluted with water (50 c.c.) and washed once with ether to remove the neutral products. The alkaline solution was acidified with HCl to p_H 2, saturated with sodium chloride and extracted with ether (25 c.c. × 4). The combined extract was washed with brine and dried. The solvent was removed and the crude acid was mixed with benzene (30 c.c.) which was distilled off to remove any moisture. The residue was refluxed with benzene (80 c.c.), alcohol (40 c.c.) and sulphuric acid (C.P., 8 c.c.) for 17 hours. This was cooled, diluted with water (100 c.c.), the solvent phase separated and the aqueous portion extracted with benzene (20 c.c. × 3). The benzene extracts were worked up as usual (*vide supra*) to give the required ester as a colorless liquid: b.p. 138-39°/1.5 mm, η_D^{29} 1.4390, yield 12.2 g. (95%).

A sample refractionated for analysis had b.p. 138-39°/1.5 mm, $\eta_D^{29.5}$ 1.4380, $d_4^{29.5}$ 0.9495, M_D 79.0 (calc. 79.3), M.W. by saponification 288.2 (calc. 286). (Found: C, 65.99; H, 10.36. $C_{16}H_{30}O_4$ requires C, 67.13; H, 10.49%).

2-Methyl-5-isopropylsuberic Acid (XIV).—The above ester (5.27 g.) was refluxed with ethanolic KOH (KOH 6 g., water 15 c.c. and ethanol 85 c.c.) for 6 hours and worked up as described for (VII). The acid was obtained as a thick liquid, yield 4.05 g. (95.6%). A sample was purified for analysis by evaporative distillation (bath temperature 160°/0.07 mm). (Found: C, 62.12; H, 9.74. $C_{13}H_{22}O_4$ requires C, 62.62; H, 9.56%).

3-Methyl-6-isopropylsuberone (III) was prepared from the above acid (XIV: 5.7 g.), iron powder (6.1 g.) and barium hydroxide (0.25 g.) in a manner described for the isomeric ketone (I). The decomposition temperature was almost the same and the ketone was obtained as a colorless liquid with a strong peppermint odour: b.p. 125°/40 mm, η_D^{25} 1.4620, yield 3.5 g. (84.1%). The properties of the analytical sample have been recorded in Table I. (Found: C, 78.49; H, 11.91. $C_{11}H_{20}O$ requires C, 78.57; H, 11.91%).

The *semicarbazone* (pyridine method) after four crystallisations from alcohol was obtained in white small needles, m.p. 154°. (Found: N, 19.0. $C_{12}H_{23}ON_3$ requires N, 18.66%).

The 2:4-*dinitrophenylhydrazone* (H_2SO_4 method) (crude: m.p. about 75°) crystallised from alcohol in deep orange plates, m.p. 97-98°. (Found: N, 16.48. $C_{17}H_{24}O_4N_4$ requires N, 16.1%).

Infra-red Spectra.—These were taken by the courtesy of Sadtler Research Laboratories (Philadelphia, U.S.A.) on pure liquids (cell width 0.01 mm, NaCl prism) on Baird Associates I.R. spectrophotometer.

DEPARTMENT OF ORGANIC CHEMISTRY,
INDIAN INSTITUTE OF SCIENCE,
BANGALORE-3.

Received September 20, 1956.

[Jour. Indian Chem.Soc., Vol.34, No. 4, 1957]

THE ELECTRICAL CONDUCTIVITY OF ALUMINIUM OXIDE SOLS

By A. K. M. Trivedi and K. M. Buch

Concentrated aluminium oxide sol has been prepared by peptising freshly precipitated aluminium hydroxide with dilute hydrochloric acid, purified by hot dialysis, and its various constituents determined. The conductivity of the sol, diluted with water, has been measured. It is concluded that bulk of the stabilising electrolyte adheres to the micelles and the sol shows the behaviour of a typical colloidal electrolyte.

According to Pauli (*Kolloid Z.*, 1921, **29**, 281), colloidal aluminium oxide contains particles of the composition $[m\mathrm{Al(OH)_3}.\ n\mathrm{AlOCl}.\ \mathrm{AlO^+Cl^-}]$. Thomas (*J. Phys. Chem.*, 1931, **35**, 27) also was of the view that the dispersed phase in the case of such sols consisted of oxolated aluminium oxychloride of the Werner type. On the other hand, no oxychloride of aluminium has been established with certainty (Weiser, "Colloid Chemistry", 2nd ed., 1949, p. 216). The particles of such sols may consist of $x(\gamma.\mathrm{Al_2O_3}.\mathrm{H_2O}).y\mathrm{HCl}.z\mathrm{H_2O}$ with $\mathrm{Al^{3+}}$ and $\mathrm{H^+}$ as stabilising ions and $\mathrm{Cl^-}$ as counter ions or gegenions*.

The nature of the stabilising electrolyte in the case of aluminium oxide sol may be investigated by electrical conductivity measurements. The conductivity of aluminium oxide sols has been determined by a number of workers (Lottermoser, *Z. Elektrochem.*, 1924, **30**, 391 ; Pauli and Schmidt, *Z. physikal. Chem.*, 1927, **139**, 199 ; Dhar and Chakravarti, *Z. anorg. allgem. Chem.*, 1927, **17**, 168 ; Mukherjee *et al.*, *Kolloid Z.*, 1933, **63**, 36 ; 1933, **65**, 72 ; this *Journal*, 1933, **10**, 405). In most cases, however, dilute sols were employed. In the present investigation the conductivity of concentrated aluminium oxide sols has been determined and a systematic investigation of the relation between conductivity and dilution has been carried out.

Experimental

Several methods have been employed by different investigators for the preparation of aluminium oxide sols (Gay Lussac, *Ann. chim. phys.*, 1810, **74**, 193 ; Graham, *Phil. Mag.*, 1862, *iv* **23**, 290 ; Schneider, *Annalen*, 1890, **257**, 359 ; Davis, *J. Phys. Chem.*, 1932, **86**, 949 ; Kohlshutter, *Z. Elektrochem.*, 1923, **29**, 253 ; Dhar and Mittra, this *Journal*, 1932, **9**, 315 ; Pauli, *loc. cit.*). In the present investigation, concentrated aluminium oxide sols were prepared by the addition of ammonium hydroxide to aluminium chloride solution and then peptising aluminium hydroxide, thus formed, by dilute hydrochloric acid, and subsequently subjecting the sol to continuous hot dialysis (Neidle and Barab, *J. Amer. Chem. Soc.*, 1916, **38**, 1962 ; 1917, **39**, 71). Purified sols were carefully evaporated on the water-bath at 60-70°. It was found that the partly dialysed sol could be concentrated up to 80 g. per litre. It was remarkable that both highly purified and impure sols had a great tendency to set to a gel condition.

*Previously the term 'gegenion' was wrongly used by us for 'stabilising ion' (e. g. Trivedi and Divatia, *Curr. Sci.*, 1952, **21**, 131).

Aluminium oxide content of the sol was determined by evaporating the sol to dryness first in the oven at 110-20° and subsequently heating to a constant weight over a burner. Anhydrous aluminium chloride, which is volatile under this condition (Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. V, 1946, p. 316), escapes, leaving only aluminium oxide. Chloride content of the sol was determined as follows: To an aliquot portion of the sol excess of the sodium sulphate was added. The coagulum was digested on a sand-bath and then filtered and washed till free of chloride. An excess of calcium carbonate was added to neutralise the acid, if any, and the solution was titrated against standard silver nitrate using potassium chromate as indicator (Cumming and Kay, "A Text-Book of Quantitative Chemical Analysis", 5th ed., 1939, p. 164).

Two sols were employed for conductivity determination. Their compositions are shown below.

TABLE I

Sol.	Al_2O_3 (g./litre).	$AlCl_3$ (g./litre).
A	37.56	0.621
B	36.92	0.665

Water (sp. condy. = 2×10^{-6} mho) was used for dilution. As the sols were highly viscous, great care was taken for preparing different dilutions. The dilutions were further checked by analysis. The conductivity of the sols, prepared as above, was measured at 35° ± 0.1° in two series. In one of them, starting with the most concentrated sol, the conductivity of the diluted sols was successively determined. In the second series, the order was reversed. For each dilution, several readings were taken. The electrical conductivity (in mho) of the sol was measured as before (Trivedi *et al.*, *Proc. Ind. Acad. Sci.*, 1952, **35A**, 53°). Table II records the mean values of the resistances at different dilutions.

TABLE II

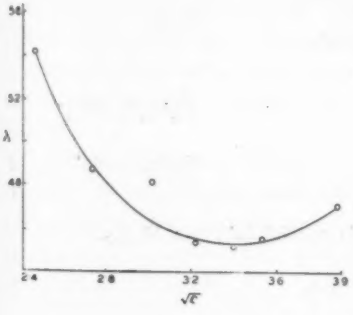
Sol. conc.	Resistance (ohms).	Sp. conduc. of micelles × 10^4.	Eq. conduc. of micelles. (*a*)	Eq conduc. of free $AlCl_3$. (*b*)	Ratio *a*/*b*.	Sol. conc.	Resistance (ohms).	Sp. conduc. of micelles × 10^4.	Eq. conduc. of micelles. (*a*)	Eq. conduc. of free $AlCl_3$. (*b*)	Ratio *a*/*b*.
		Series A.						Series B.			
37.56	330.6	6.645	47.5	143	0.33	36 92	310.4	7.076	47.1	142	0.33
34.14	371.5	5 913	46.5	145	0.32	30.75	385 4	5 699	45.6	145	0.31
28 88	440.3	4.989	46.6	147	0.31	28 39	421.4	5.214	45 2	146	0 30
26 81	475.5	4. 19	46 6	148	0 31	26 35	451 1	4.871	45 4	147	0 31
25.01	515.5	4.262	45.8	149	0 30	22 15	507.2	4 332	48.1	150	0.32
18 78	659 7	3 330	47 5	151	0.30	18 45	601.1	3.655	48.7	153	0 31
9.390	1009	2 183	62.3	166	0.37	14 76	676.2	3.249	54 1	156	0 34
3 765	2408	0.912	65.1	180	0.36	3.692	2186.6	1.005	66 7	179	0.37

Discussion

The aluminium oxide sol may contain aluminium oxide, aluminium chloride and HCl; the latter two may be both in the free as well as in the combined state. On testing, free H^+ and Al^{3+} were found to be absent, Al^{3+} ion being tested with 8-hydroxyquinoline (Berg., *Z. anal. Chem.*, 1927, **71**, 369). Hence, it may be concluded that aluminium chloride is the only stabilising electrolyte under the experimental conditions and most of it is present in the combined state. Assuming that conductivity of the sol is due to micelles only, the equivalent conductivity of the micelles can be found out. The molecular conductivity of aluminium chloride in the free state has been obtained from the data of Jones (Carnegie Institution of Washington, Publication No. 170, 1912) and Bjerrum (*Z. physikal. Chem.*, 1907, **59**, 336). Table II shows the equivalent conductivity of the micelles, of free aluminium chloride ($\frac{1}{4}$ molecular conductivity) and the ratio of the two.

In all cases, it is obvious that the eq. conductivity of the micelles is much smaller than that of free aluminium chloride, the actual ratio being about 0.3 to 0.4. Hence, the bulk of the stabilising electrolyte adheres to the micelles, the behaviour being similar to that of sulphur sol (Bolam and Trivedi, *Trans Faraday Soc.*, 1943, **39**,247), iron oxide sol (Trivedi *et al., loc. cit.*) and chromium oxide sol (Trivedi, Bhatt and Divatia, this *Journal*, 1956, **33**, 116). In the case of aluminium oxide sol, again, the degree of dissociation of the stabilising electrolyte appears to be rather high as in the case of chromium oxide sol. The higher value may be due to the fact that the sol may contain free electrolyte, not allowed for in the calculations. At any rate, the bulk of the stabilising electrolyte adheres to the micelles. If we compare the variation of the conductivity of the micelles, on dilution, with the variation of the conductivity of free aluminium chloride on similar dilution, it is found that unlike the free electrolyte, the eq. conductivity of the micelles first decreases and then increases on further dilution. This is shown graphically in the case of sol B. The behaviour of aluminium oxide sol is in harmony with that shown by iron oxide and chromium oxide sols (*loc. cit.*). Hence, like soap solutions, such systems may be classified amongst colloidal electrolytes (McBain, *J. Amer. Chem. Soc.*, 1928, **50**, 1636).

Fig. 1



The thanks of the authors are due to the Ahmedabad Education Society for a generous grant towards chemicals and apparatus.

Chemistry Department,
L. D. Arts College & M. G.
Science Institute, Ahmedabad-9.

Received October 29, 1956.

[Jour. Indian Chem. Soc., Vol. 34, No. 4, 1957]

ISOLATION OF URSOLIC ACID FROM *VINCA ROSEA* LINN.

By S. Roy and A. Chatterjee

Ursolic acid, a 2-hydroxy-17-carboxy acid of α-amyrin series, has been isolated from the whole plant of *Vinca rosea* Linn.

During the isolation of alkaloidal constituents from the whole plant of *Vinca rosea* Linn., a considerable amount of a light yellowish green amorphous solid was obtained. It has been now possible to isolate from the latter a triterpene derivative of α-amyrin series (yield 0.1%), proved to be identical with ursolic acid by direct comparison of their properties (Table I).

TABLE I

	Ursolic acid from *Vinca rosea L.*	Ursolic acid from *Verbena stricta**
M. P.	280°	282°
Mol. formula	$C_{30}H_{48}O_3$	$C_{30}H_{48}O_3$
Optical rotation	$[\alpha]_D^{28°} = +65°.8$	$[\alpha]_D^{28°} = +65°.6$
Crystalline form	Fine needles from ethyl alcohol.	Same.
Solubility	Insoluble in benzene, chloroform and soluble in acetone, ethyl acetate and ethyl alcohol.	Same
Colour reactions	In Liebermann and Burchard's test the chloroform layer turns pink which immediately changes to blue and on keeping turns green.	Same
Mol. formula and m.p. of methyl ursolate	$C_{31}H_{50}O_3$, 169°	$C_{31}H_{50}O_3$, 168.4°
Mol. formula and m.p. of acetylursolic acid	$C_{32}H_{50}O_4$, 263°	$C_{32}H_{50}O_4$, 282°

* King, Chatterjee and Parks, *J. Amer. Pharm Assoc., Sci. Ed.*, 1950, **39**, 595.

*EXPERIMENTAL

The dried and milled drug (1.0 kg.) was extracted with alcohol. The green alcoholic extract deposited an amorphous mass (A). The concentrated extract when poured into water deposited a further amount of solid materials (B). The supernatant reddish brown liquid was decanted off and worked up for the alkaloids (Chatterjee and Talapatra, *Science & Culture*, 1955, **20**, 568).

Isolation of Ursolic Acid.—The light yellow amorphous fractions (A) and (B) (2.0 g.) were dissolved in alcohol and the alcoholic solution was treated with charcoal

* All the melting points recorded here are uncorrected.

and filtered. From the clear filtrate colorless needles (1.2 g., m.p. 268-74°) of ursolic acid separated out on cooling. On recrystallisation from alcohol fine needles of ursolic acid (m. p. 280°) were obtained. Further purification of the substance was done by its chromatography over alumina.

Ursolic acid (0.1 g.), dissolved in a mixture of ethyl acetate and acetone (2 : 1), was adsorbed in neutral alumina (32 cm × 2 cm). The chromatogram was developed and eluted with benzene and a mixture of benzene and ethyl acetate (Table II).

TABLE II

Eluents.	Fractions.	Residue on evaporation.
Benzene	1-5	Nil
Benzene+10% ethyl acetate	6-10	Nil
Ethyl acetate	10-13	Nil
Ethyl acetate +5% alcohol	13-20	White solid, m p 280°

Fractions (13-20) crystallised from a mixture of ethyl acetate and ethyl alcohol (1 : 1) in fine needles (yield 0.083 g.), m.p. 280°. (Found : C, 78.52 ; H, 10.64. Calc. for $C_{30}H_{48}O_3$: C, 78.95 ; H, 10.52%).

An alcoholic solution of the substance showed no characteristic change in colour with ferric chloride solution nor did it liberate iodine when a solution of ursolic acid was added to a solution of a mixture of potassium iodide and potassium iodate. The optical rotation of ursolic acid was observed in 1*N* alcoholic KOH solution.

Acetyl Derivative.—Ursolic acid (0.1 g.) was refluxed with freshly distilled acetic anhydride (5 c.c.) and pyridine (3 drops) for 5 hours. The reaction product was then added to crushed ice. The white flocculent mass separating was crystallised from dilute methyl alcohol when fine needles of acetylursolic acid (yield 0.095 g., m.p. 283°) were obtained. (Found : C, 77.50 ; H, 9.97. Calc for $C_{32}H_{50}O_4$: C, 77.10 ; H, 10.04%).

Methyl Ursolate.—Ursolic acid (0.1 g.) on methylation with diazomethane in methanol furnished silky needles of its methyl ester (yield 0.07 g.), m.p. 112-14°. It was subsequently purified by chromatographic resolution over alumina (25 cm × 2 cm) using petroleum ether (b.p. 60-80°) and benzene as eluents, collected in fractions of 15 c.c. each (Table III).

TABLE III

Eluents.	Fractions.	Residue on evaporation.
Pet. ether	1	Nil
Do	2-5	Non-crystallisable slimy mass.
Do	6-7	Nil
Benzene	8	White solid, m.p. 162°
Do	9-12	White solid crystallised from methanol ; m.p 168°
Do	13-15	Nil

Fractions 8-12 were all mixed together and crystallised from dilute methanol (50%) when silky needles of methyl ursolate separated (yield 0.06 g.), m.p. 169°. (Found : C, 79.43 ; H, 10.92 ; OMe, 6.54. Calc. for $C_{31}H_{50}O_3$: C, 79.57 ; H, 10.63 ; OMe, 6.59%).

Benzoyl Derivative.—Ursolic acid (0.2 g.) was refluxed with benzoyl chloride (5 c.c.) and pyridine (0.1 c.c.). The reaction product was poured into crushed ice when a white flocculent mass separated. It was crystallised from benzene in colorless crystals with sandy touch (yield 0.05 g.), m.p. 216-18°. (Found : C, 79.64 ; H, 9.56. $C_{37}H_{52}O_4$ requires C, 79.28 ; H, 9.28%).

The authors take the opportunity to offer their sincere thanks to Mr. S. P. Sen, the Manager, Bengal Chemical and Pharmaceutical Works Ltd., Calcutta for financial help to one of them (S. Roy) and encouragement without which it would not have been possible for them to carry out this work.

Department of Organic Chemistry,
University College of Science and Technology,
Calcutta.

Received December 5, 1956.

SHORT NOTES

AQUO-AMMINO ANTIMONY CHLORIDE

By H. K. Das and S. Pani.

Antimony chloride has been reported to absorb ammonia in molten condition with the formation of monoammino-, diammino- and triammino- antimony trichloride (Deherain, *Compt. rend.*, 1861, **52**, 734). A saturated aqueous solution of antimony trichloride containing hydroxo-trichloro antimonite and aquo-trichloro antimony complexes has been found to react with suitable chelates or neutral molecules like pyridine (Pani *et al.*, this *Journal*, 1956, **33**, 537, 538). It is therefore expected that ammonia would react with such a solution.

The chemicals used were of Analar quality reagents. Three different samples were prepared by slightly altering the conditions, as described below.

Compound (I).—A small amount of a saturated aqueous solution of antimony trichloride in a beaker was exposed to concentrated ammonia in a bottle inside a bell jar. Ammonia was immediately absorbed with the formation of a white compound. It was stirred from time to time and allowed to stand for over 16 hours when the whole mass became solid. It was powdered and repeatedly washed with ether, filtered and dried over sulphuric acid in a vacuum. The material when heated melts, and gives off ammonia and a white sublimate. It is very little soluble in water and the solution in hot water just responds to the tests of antimony and chloride. It is insoluble in ether but dissolves in sodium hydroxide with the liberation of ammonia.

Compound (II).—A small amount of a saturated aqueous solution of antimony chloride with 25 to 30 c.c. of ether was exposed to ammonia as before in a bell jar. The reaction started immediately and the product obtained after four hours was washed, filtered and dried as before. The properties are similar to those of the compound (I). The analytical results are shown in the table below.

Table I

Compound.	% Sb.	% Cl.	% NH.	% HO.
Compound (I)	41.03	36.16	14.54	8.27
Compound (II)	43.42, 43.33	37.62, 38.04	11.91, 11.81	7.05, 6.82
Compound (III)	46.51, 46.45	40.54, 41.09	7.85, 7.87	5.1, 4.5
Calc. for				
$SbCl_3(NH_3)\,H_2O$	46.26	40.46	6.46	6.84
$SbCl_3(NH_3)_2\,H_2O$	43.45	38.00	12.13	6.42
$SbCl_3(NH_3)_2\,H_2O$	40.98	35.79	17.17	6.06

Compound (III).—A solution of antimony chloride in ether (containing no water) was exposed to ammonia as before and there was no evidence of the formation of any

solid compound even after four to five hours; only a very thin white film was observed on the side of the beaker. After 24 hours the solution became more dense, viscous and turbid, but there was no solid phase. No solid phase appeared even after 48 hours. After three days a solid separated out which was filtered, washed and dried as before. The properties of this compound were also similar.

Compound (I) is most probably $SbCl_3(NH_3)_3.H_2O$ with a small amount of the compound (II) which is $SbCl_3(NH_3)_2.H_2O$. The compound (III) is probably formed due to absorption of water besides the absorption of ammonia, and since the concentration ot water vapour is small compared to that of ammonia inside the bell jar, the formation of this compound is slow. The complex (III) is therefore, $SbCl_3.NH_3.H_2O$. It is of interest to note that the complex (III), which is formed after three days, contains only one molecule of ammonia per atom of antimony, whereas, the other two, which are comparatively quickly formed under similar conditions, contain more ammonia. The ammonia and water molecules are strongly bound as they are not lost over concentrated sulphuric acid (the compound II when kept over sulphuric acid lost 0.03% in weight after three months).

These compounds are possibly co-ordination complexes.

DEPARTMENT OF CHEMISTRY,
RAVENSHAW COLLEGE,
CUTTACK-3.

Received October 31, 1956.

[Jour. Indian Chem. Soc., Vol. **34**, No. 4, 1957]

EFFECT OF AZOTOBACTER ON FIXED NITROGEN

BY M. A. AZIM AND FAZAL MOHYUDDIN

The utilisation of fixed nitrogen by *Azotobacter vinelandii* has been investigated by using a colorimetric method. It has been found that only those nitrogenous compounds are utilised by the bacteria which are likely to be reduced to ammonia, and that the lag period of the bacteria in case of compounds utilised increases with increase of concentration.

Horner (*J. Bakt.*, 1944, **47**, 1) and Rosenblum (*ibid.*, 1952, **61**, 475) investigated the effect of various nitrogenous compounds including amino-acids, amines, amides, glycocoll, urea and hydrazine on the growth and nitrogen-fixing activities of azotobacter. They found that with the exception of urea these were not as readily utilised as the inorganic ammonium salts and nitrates.

Fuller and Rettger (*Soil Sci.*, 1931, **31**, 219) observed that more complex organic compounds were not easily attacked by azotobacter and consequently the growth and nitrogen-fixing activity of the organism were not much influenced.

Lewis and Hinshelwood (*J. Chem. Soc.*, 1948, 824) and Azim and Roberts (*Biochim. biophys. Acta*, 1955, **18**, 363) have established that inorganic ammonium salts, nitrates and nitrites are utilised by *Azotobacter vinelandii*.

Thus, those nitrogenous compounds, which are reduced to ammonia, are likely to be utilised by azotobacter, and this view conforms with the ammonia hypothesis of biological fixation of atmospheric nitrogen (Wilson, *Ann. Rev. Biochem.*, 1945, **14** 685). In order to confirm our own point of view we undertook to investigate a few organic and inorganic nitrogenous compounds like potassium nitrate and amyl nitrite, which are reduceable to ammonia, and some other compounds like nitrobenzene, aniline and sodium azide, which are not reduceable to ammonia, and we found our hypothesis to be correct.

Various workers investigated the utilisation of compounds without studying their relation with concentration. We have therefore attempted to investigate the speed of utilisation at different initial concentrations and have obtained a relation between concentration and the lag period of the bacteria.

Procedure.—The flasks containing identical volumes of the sterile culture medium inoculated with a known propulation of *A. vinelandii*, usually about 10⁹ cells per 25 c.c., were incubated at 30°. The calculated volume of standard substrate solution was added to the culture medium so as to attain the desired concentration (10^{-4} *M* to 10^{-2} *M*). A known volume of the test solution was withdrawn by means of a pipette and analysed by the usual colorimetric methods (nitrate with phenol disulphonic acid, nitrite with Griess Ilosva's reagent, aniline with bleaching powder and azide with ferric chloride).

TABLE I

% Utilisation.

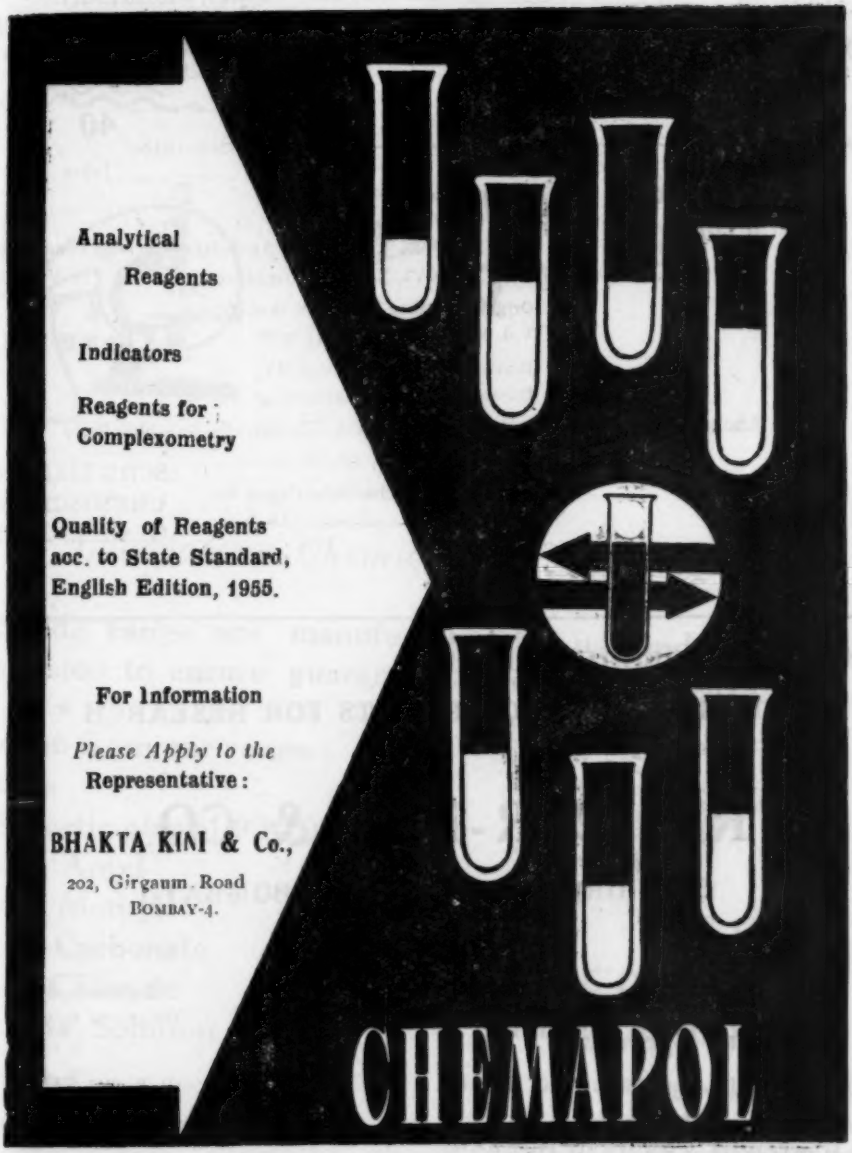
	Potassium nitrate.		Amyl nitrite.				Pot. nitrate	Amyl nitrite.	
Time.	$10^{-2}M$.	$10^{-3}M$.	$10^{-2}M$.	$10^{-3}M$.	$10^{-4}M$.	Time.	$10^{-2}M$.	$10^{-2}M$.	$10^{-3}M$.
0.0 hr.	0.0	0.0	0.0	0.0	0.0	7.0 hr.	0.0	82.2	0.0
1.5	0.0	0.0	0.0	0.0	0.0	7.5	5.4	100.0	0.0
2.0	0.0	0.0	0.0	0.0	9.1	8.0	0.7	...	0.0
2.5	0.0	0.0	0.0	0.0	19.6	8.5	21.7	...	0.8
2.75	0.0	0.0	0.0	0.0	58.8	9.0	...	...	13.3
3.0	0.0	0.0	0.0	0.9	100.0	10.0	32.5	...	36.8
3.5	0.0	0.0	0.0	4.0		10.5	48.7	...	69.4
4.0	0.0	0.0	0.0	11.8		11.5	62.2	...	...
4.5	0.0	14.3	0.0	37.5		12.0	...	...	100.0
5.0	0.0	28.6	0.0	100.0		12.5	83.8	...	...
6.5	0.0	71.5				13.5	100.0	...	

The utilisation of potassium nitrate, amyl nitrite, nitrobenzene, aniline and sodium azide by *Vinelandii* was studied at different concentrations ranging from 10^{-4} *M* to 10^{-2} *M*. Potassium nitrate and amyl nitrite were found to be utilised in solutions lower than 2×10^{-2} *M* concentrations, while in stronger solutions they were neither utilised nor were found to be toxic. It is clear from the table that the lag period

required by azotobacter to start utilisation of nitrates and nitrite increases with increase of concentration and after the expiry of the lag period the rate of utilisation increases with increase of concentration. Nitrobenzene, aniline and sodium azide were not utilised even at lower concentrations. From these results it is concluded that nitrobenzene, aniline and azide although containing the same groups as of nitrite and ammonia are not utilised because they are not reduceable to ammonia and thus the ammonia hypothesis of nitrogen fixation has been confirmed.

CHEMISTRY LABORATORIES,
GOVERNMENT COLLEGE,
LAHORE.

Received November 11, 1956.



PRAHA, CZECHOSLOVAKIA

HELVETICA
CHIMICA
ACTA

SCHWEIZERISCHE
CHEMISCHE GESELLSCHAFT
Verlag Helvetica Chimica Acta
Basel 7 (Schweiz)

Seit 1918 **40** Jahre

Es sind noch lieferbar:

Neudruck zum Teil ab Lager
Vol. I-XIV (1918-1931)
Vol. XVII-XX (1934—1937) Auslieferung erfolgt demnächst!
Vol. XV, XVI, XXI-XXV (1932, 1933, 1938-1942) in Vorbereitung

Originalausgaben, zum Teil druckfrisch
Vol. XXVI-XXXIX (1943-1956)

Diverse **Einzelhefte** ab Vol. XV
Preise auf Anfrage. Nur solange Vorrat

Abonnemente:

laufender Jahrgang Vol. XL (1957) Fr. 80.—plus Porto

Das wissenschaftliche Organ der SCHWEIZERISCHEN CHEMISCHEN GESELLSCHAFT

*** FOR YOUR REQUIREMENTS**
OF ALL KINDS OF EQUIPMENTS FOR RESEARCH *

RAJ-DER-KAR & CO.,

231, HORNBY ROAD, FORT, BOMBAY-1

Telephone : 26-2304
Telegram : 'TECHLAB'.

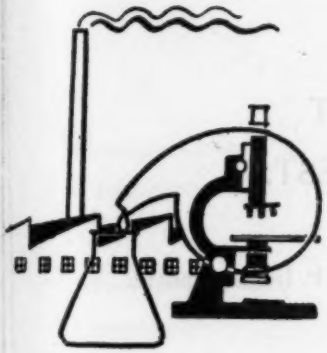
A few of our Agencies :

* LUDWIG SEIBOLD, Austria,
For p_H Testers, Titrators,
and Recorders etc.

* EASTMAN KODAK U. S. A.,
For All Sorts of Complex
Organic Chemicals.

* W.A. TAYLOR & CO., U. S. A.
For p_H Comparators, Indicators,
Water Analysers etc.,

* TRACERLAB Inc., U. S. A.,
For Radiochemicals & Equipment
for Nuclear Research.



SERVING for LAST 40 YEARS

Laboratory Chemicals & Reagents

of a wide range are manufactured by us under expert supervision to ensure guaranteed standard & reliability.

A selection from our range :

Acetone
Acid Acetic glacial 99-100%
Alcohol Amyl
Alcohol Methyl
Barium Carbonate
Barium Chloride
Benedicts' Solution
Benzene
Carbon Tetrachloride
Lead Acetate
Liquor Ammon Fort (24/27%)
Magnesium Sulphate XL

THE CALCUTTA CHEMICAL CO., LTD.

HEAD OFFICE: 35, Panditia Road, Calcutta 29.

BRANCH OFFICES & DEPOTS AT : Delhi, Madras, Bombay, Bangalore, Vizag., Nagpur, Jamshedpur, Patna, Ranchi, Bhagalpur, Madhupur, Asansol, Siliguri.

SPECIALLY MADE

Apparatuses

For

* BOILING POINT TEST

* FREEZING POINT TEST.

* ARSENIC TEST.

B. P. (1953) Standard.

Please Enquire to

SCIENTIFIC GLASS APPARATUS MFG. CO.

11/2 Harinath Dey Road, Calcutta-9

Phone : East 4411. Gram : Siganiko,

BOROSIL

LABORATORY GLASSWARE

such as

FLASKS, BEAKERS, CONDENSERS, MEASURING FLASKS, MEASURING CYLINDERS, PIPETTES & ANY SPECIAL APPARATUS MADE-TO DESIGN

and

PENICILLIN VIALS, VACCINE BULBS—WHITE & AMBER

ALL OTHER APPARATUS & EQUIPMENT MANUFACTURED TO CLIENT'S DESIGN

INDUSTRIAL & ENGINEERING APPARATUS CO. PRIVATE LTD.

CHOTANI ESTATES, PROCTOR ROAD GRANT ROAD, BOMBAY 7.

****LABORATORY "PYREX" GLASSWARE****

Available from ready stock

* Beakers
* Flasks
* Test-tubes
* Reagent Bottles
* Glass Tubing
* Glass Roding

For further details please contact:

LABORATORY FURNISHERS

DHUN MANSION, VINCENT ROAD, DADAR, BOMBAY 14.

Grams: 'LABFURNISH' BOMBAY-DADAR. Phone: 62761.

Branch: AHMEDABAD.

For Laboratory *Reagent Quality* Acids

To Precise Specifications

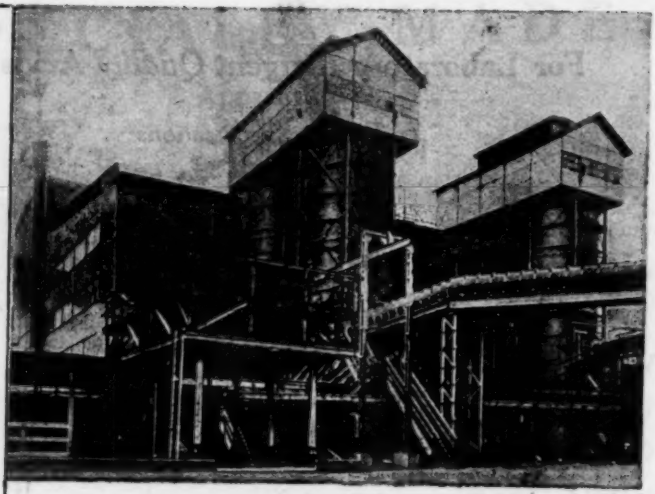
Maximum Limits of Impurities:	Acid Sulphuric H_2SO_4 :98% w/w Sp. gr. 1.840 at 15°.	Acid Nitric HNO_3:69.8% w/w Sp.gr. 1.420 at 15°.	Acid Hydrochloric HCl:35.39% w/w Sp. gr. 1.8 at 15°.
Non-Volatile Matter :	0.0025 %	0.001 %	0.0015 %
Chloride (Cl) :	0.0003 %	0.0001 %	—
Free Chlorine (Cl) :	—	—	0.0002 %
Nitrate (NO_3) :	0.00002 %	—	—
Iodate (IO_3) :	—	0.0005 %	—
Sulphate (SO_4) :	—	0.0003 %	0.0003 %
Heavy Metals (Pb) :	0.0002 %	0.0002 %	0.0002 %
Iron (Fe) :	0.0001 %	0.0001 %	0.0001 %
Arsenic (As_2O_3) :	0.00001 %	0.05 part per million	0.04 part per million
Ammonia (NH_3) :	0.0005 %	—	—
Oxygen Absorbed (O) :	1.0001 %	—	—

We invite orders and enquiries.
Write us about your requirements for other reagent quality chemicals.

Bengal Chemical & Pharmaceutical Works, Ld.

CALCUTTA :: BOMBAY :: KANPUR

Office : 6, Ganesh Chunder Avenue, Calcutta-13



WE DESIGN
DELIVER &
ERECT

COMPLETE EQUIPMENT FOR H_2SO_4 PRODUCTION

WE SHALL OFFER TO YOU TECHNICAL UNITS
OF THE FOLLOWING OUTPUTS:

Raw material: SULPHUR	10 mt/24 hrs.	PYRITE	50 mt/24 hours
	25 mt/24 ,,		100 mt/24 ,,
	50 mt/24 ,,		150 mt/24 ,,

WE SHALL GUARANTEE A SUITABLE
AND UP-TO-DATE DESIGN AND ECONOMIC OPERATION

TECHNOEXPORT

Praha—Czechoslovakia

For informations please contact

TRADE REPRESENTATION OF CZECHOSLOVAK REPUBLIK,

BOMBAY BRANCH: KASTURI BUILDING, JAMSHEDJI TATA ROAD, BOMBAY.

CALCUTTA BRANCH: P-38, MISSION ROW EXTN, CALCUTTA.

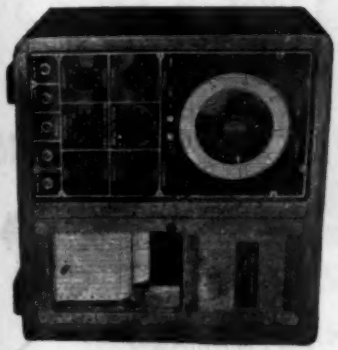
FOR RAPID & ACCURATE CHEMICAL ANALYSIS

USE

TINSLEY

POLAROGRAPH (with derivative circuit)

Here are some advantages:



* MICRO ANALYSIS
* HIGH SENSITIVITY
* QUALITATIVE AND QUANTITATIVE ESTIMATION
* SIMULTANEOUS ESTIMATION OF SEVERAL CONSTITUENTS ON ONE POLAROGRAM
* ADAPTABILITY: ANALYSIS OF METALS, ORGANIC & INORGANIC SUBSTANCES ON THE SAME SAMPLE
* REPEATED ANALYSIS
* SIMPLIFIED OPERATION FOR USE BY SEMI-SKILLED STAFF
* ROUTINE ANALYSIS WITH SPEED AND ACCURACY.

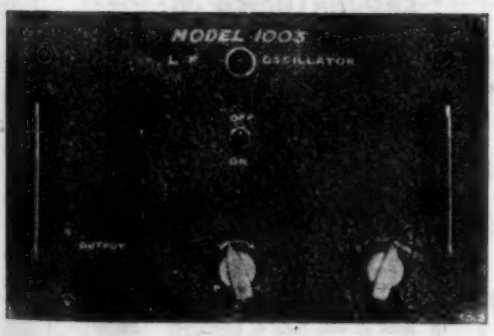
For further particulars, please contact Sole Agents in India

PIONEER EQUIMENT CO. PRIVATE LTD.

(Formerly Pioneer Industries

1, Mango Lane, CALCUTTA-1. | 139, Medows Street, (Ground Floor) BOMBAY-1. | 193, Mount Road MADRAS-2.

ELECTRONIC INSTRUMENTS FOR CHEMICAL LABORATORIES



1003 is a twin-T type oscillator for Bridge measurement. Excellent wave form, distortion less than 3%, adequate power, adjustable up to 2.5 watts. max. Oscillator frequency 500, 1000 and 2000 cps.

Also Available:

Apparatus for measurement of dielectric polarisation using heterodyne beat principle.

EMISSION RADIO & VARIETIES.

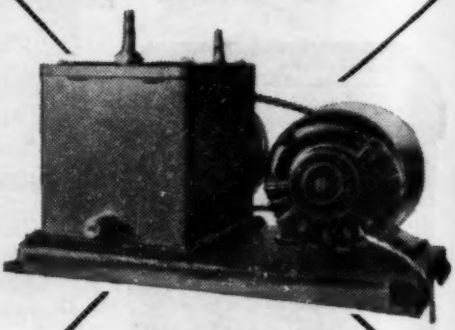
120, LOWER CIRCULAR ROAD, CALCUTTA 14.

Phone—24-2513

All In One
INDEX
REAGENT BOTTLES
made by
Sigcol

Sole Distributors
GHARPURE & CO.
P36, ROYAL EXCHANGE PLACE
EXTENSION • CALCUTTA-1
GRAM: MEEHAMO PHONE: 22 2061

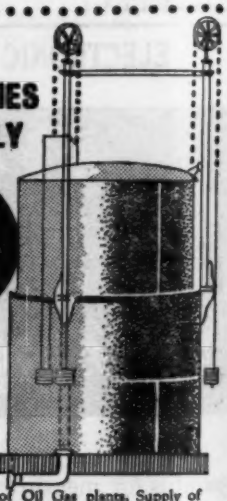
MADE IN INDIA
HIGH VACUUM ROTARY PUMP
Single Stage & Two Stage
Suitable for Laboratory use and similar in performance to those made in Germany, England & U. S. A.



All Indian Materials and Constructions.
BASIC & SYNTHETIC CHEMICALS PRIVATE LTD
P. O. Jadavpur College, Calcutta-32

GS Gas PLANTS
FOR
HEATING
IN
LABORATORY
INDUSTRY
KITCHEN
GANSONS
PRIVATE LIMITED.
P.O.B. 5576, BOMBAY 14.
——Also makers of——
Superior Laboratory Fittings
Atomic Equipments.

For
LABORATORIES
GAS SUPPLY
OIL GAS PLANT



—a must for a modern Laboratory and Industry. We have at our back an experience of many a years in serving Laboratories & Industrial concerns all over India & abroad.

Our Specialities—Fitting of Oil Gas plants, Supply of Science Laboratory Equipments, Furniture & Wood work of all descriptions.

MANSFIELD OIL GAS CO. LD
16, RADHANATH CHOWDHURY ROAD, CALCUTTA-12
Branch—301, LINGHI CHETTY ST., MADRAS 1.

Phone—34-3176. Telegrams—Nadiachemi.

NADIA CHEMICAL WORKS PRIVATE LTD.

C 44, 45 & 46, COLLEGE STREET MARKET, CALCUTTA

Manufacturers of :—

1. *CHEMICALS*—**Benzene, Toluene, &c., Bromine, Halogen derivatives of both Organic and Inorganic compounds and other fine Laboratory Chemicals.**
2. **STILLS for distilling Essential Oils, Alcohols, Water, etc.**

   RECTIFIERS, CONDENSERS, &c.
3. **OVENS, Baths &c for Gas, Oil or Electric heatings.**
4. **Scientific Apparatus (PHYSICAL, CHEMICAL, BIOLOGICAL, &c.) of both Glass and Metal.**
5. **MICRO-ANALYSIS APPARATUS.**

Please ask for Estimates.

PUBLICATIONS WANTED

The following publications are required for the Library of the Indian Chemical Society. These may be purchased or received in exchange with the publications of the Society.

1. Journal of the Chemical Society, London :
   1936, pp. 1-872; 1950—July to Dec. and Index; 1951, pp. 2807 to end with Index.
2. Journal of the Pharmaceutical Society of Japan :
   Available back volumes up to 1955.
3. Journal of the American Chemical Society :
   Vols. 1-32; Vol. 34, January-June (1912); Vol. 36, July-Dec. (1914); Vol. 37, January to June (1915); Vol. 53, January-April (1931).
4. Archiv der Pharmazie :
   Vol. 240 (1902); Vols. 257-259 (1919-1921); Vols. 278-289 (1940-56).
5. Berichte der deutschen chemischen Gesellschaft :
   Vol. 68 (1935), Part I; Vol. 72 (1939), Part II; and all subsequent volumes.
6. Journal of Chemical Education, U. S. A. :
   Vols. 1-6 and Vol. 11.
7. Chemical Review, U.S.A.
   Vols. 1-11, Vol. 15 (1934), Vol. 17 (1935) and Vol. 30 (1942).

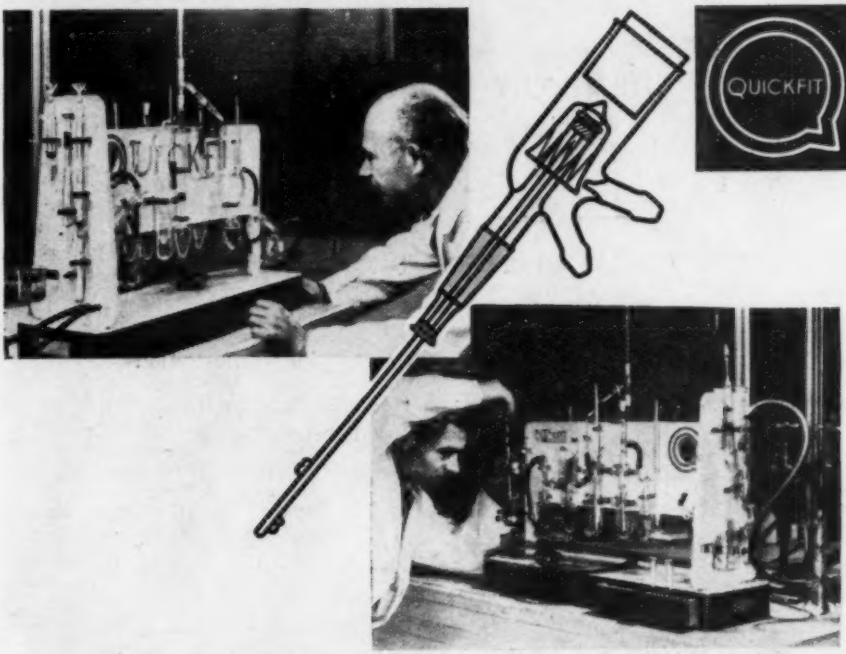
Please communicate with

THE HONY SECRETARY

INDIAN CHEMICAL SOCIETY

92, Upper Circular Road,
Po. Box No. 10857,
Calcutta—9, INDIA.

WHAT'S *NEW* IN "QUICKFIT" ?



QUICKFIT SEMI-MICRO ORGANIC PREPARATION SETS WITH SEMI-MICRO STIRRER.

1. They are strong, safe and compact and always ready for use
2. They save you chemicals, gas, filter paper, space and above all time.
3. The Stirrer is suitable for fitting directly to the 25ml reaction flask and can be driven by vacuum pump, compressed air or water.

ACCREDITED DISTRIBUTORS:

UNION SCIENTIFIC SYNDICATE

DEVKARAN MANSION, 71, PRINCESS STREET
BOMBAY 2

Tel : 28465 Gram : 'PETROLIUM'

A Monumental Work *Published March 1956*

A book that should find place on the shelves of every Library

HISTORY OF CHEMISTRY IN ANCIENT & MEDIEVAL INDIA

Incorporating

HISTORY OF HINDU CHEMISTRY

by Acharya Prafulla Chandra Ray

Edited by PROF. P. RÂY

Royal 8*vo*. Rexin bound, 494 pages with 39 illustrations.

Price *ex*-postage: Prime Edition:—Rs. 24/- (Inland), Ordinary Edition—Rs. 20/- (Inland)
£ 2/- or $ 6.00 (Foreign)

For Fellows „ „ Rs. 20/- „ „ Rs. 16/-

An invaluable book for students of science and history and to all persons interested in the scientific heritage of India.

PUBLISHED BY THE INDIAN CHEMICAL SOCIETY

92, Upper Circular Road, Calcutta-9, INDIA.

Some Opinions:

Nature, January 5, 1957.

"Since there is much new material in the book, all those who are fortunate enough to have the earlier edition will wish to have the new one. ... ...

All those interested in the History of Chemistry owe a debt of gratitude to Prof. P. Rây and the Indian Chemical Society for its publication".

J. R. Partington.

Journal of Chemical Education, February, 1957:

" ..... Professor Ray, in his carefully constructed revision of Prafulla Chandra Ray's standard 'History of Hindu Chemistry' has given us a highly informative and interesting description of Indian Chemistry. In chronological order, the contributions of Indian chemistry have been recorded from the Harappa period of the fourth millennium B.C. to the end of Mogul culture..... Many of the ideas described make delightful reading for the average chemist with a historical bent..... chemists and historians of chemistry will find in this book a valuable assessment of ancient Indian chemistry and culture".

PRESIDENT :

P. K. Bose, D.Sc., F.N.I.

VICE-PRESIDENTS :

(who have filled the office of President)

N. R. Dhar, D.Sc., Dr.rs.Sc., F.R.I.C., F.N.I.
B. B. Dey, D.Sc., F.R.I.C., F.N.I.
Sir J. C. Ghosh, Kt., D.Sc., F.N.I.
B. C. Guha, D.Sc., Ph.D., F.N.I.
P. C. Guha, D.Sc., F.N.I.
J. N. Mukherjee, C.B.E., D.Sc., F.A.S.B., F.N.I.
Mata Prasad, D.Sc., F.R.I.C., F.N.I.
J. N. Ray, O.B.E., D.Sc., F.R.I.C., F.N.I.
P. Rây, M.A., F.N.I.
B. K. Singh, Sc.D., F.R.I.C., F.N.I.

VICE-PRESIDENTS :

U. P. Basu, D.Sc., F.N.I.
B. Sanjiva Rao, D.Sc., Ph.D., F.N.I.
K. Venkataraman, D.Sc., Ph.D., F.R.I.C., F.N.I.
R. D. Desai, D.Sc., F.R.I.C., F.N.I.
President of Ahmedbad Branch (*ex-officio*)

HONY. SECRETARY :

S. K. Mukherjee, D.Sc.

HONY. TREASURER :

B. N. Ghosh, D.Sc., F.N.I.

MEMBERS OF THE COUNCIL :

N. Adhikari, M.Sc.
D. K. Banerjee, D.Sc.
D. Chakravarti, D Sc., F.N.I.
Mrs. Ashima Chatterjee, D.Sc.
B. Chatterjee, D.Sc.
A. C. Chatterji, D.Sc., Dr. Ing., F.N.I.
H. N. Das Gupta, D.Sc.
S. S. Joshi, D.Sc., F.R.I.C., F.N.I.
T. N. Ghosh, D.Sc., F.N.I.
J. Gupta, D.Sc.
A. N. Kappanna, D.Sc , F.N.I.
R. P. Mitra, D.Sc., F.N.I.
S. M. Mukherji, D.Sc., Ph.D.
P. V. Nair, M.Sc., D.Phil.
A. B. Sen, M.Sc., Ph.D.
V. Subrahmanyan, D.Sc., F.R.I.C , F.N.I.
L. M. Yeddanapalli, M.A., Ph.D., D.Sc., F.R.I.C.
S. H. Zaheer, M.A., Ph.D.

HONY. EDITORS :

S. R. Palit, D.Sc., F.R.I.C., F.N.I.
R. C. Shah, D.Sc., F.N.I.

BOARD OF ASSOCIATE EDITORS :

D. K. Banerjee, D.Sc.
P. K. Bose, D.Sc., F.N.I.
B. Chatterjee, D.Sc.
J. K. Chowdhury, M.Sc., Ph.D., F.N.I.
P. C. Dutta, D.Sc.
B. N. Ghosh, D.Sc., F.N.I.
J. C. Ghosh, D.Sc., F.N.I.
A. N. Kappanna, D.Sc., F.N.I.
S. K. Mukherjee, D.Sc.
B. C. Guha, D.Sc., Ph.D., F.N.I.
P. Ray, M.A., F.N.I.
T. R. Seshadri, M.A., Ph.D., F.N.I.
P. B. Sarkar, Dr.es. Sc., F.N.I.
K. Venkataraman, D.Sc., Ph.D., F.N.I.

HONY. AUDITORS :

P. C. Nandi, M.A., B.Sc., A.C.A.R.A.
A. B. Gupta, B.Sc., L.L.B., A.C.A.R.A.

Asst. Secretary:
B. C. Roy, M.Sc.

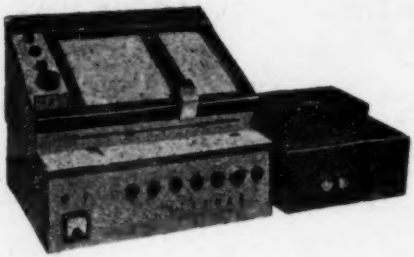
Asst. Editor :
G. Banerjee, M.Sc.

Regtd. No. C1878

We Offer

EX: BECKMAN INSTRUMENTS INC. U.S.A.

DK 2 ULTRAVIOLET-NEAR INFRA RED SPECTROPHOTOMETER



This Ratio Recording Spectrophotometer has a unique combination of the true double beam principle with single photo receiver and amplifier, utilising a high Frequency Beam Chopper and switching system. It exploits such advantages of ratio recording as free from drift and line variations and at the same time avoids the problem of photo tube matching and ageing.

Range : 200—3,000 mμ.

Resolution : 0.3 mμ at 220 mμ, 2.5 mμ at 1000 mμ
5 mμ at 2,500 mμ.

Other instruments : Infra Red Spectrophotometers, IR2A and IR4, Model B Spectrophotometer for Visible Region, Model DU for UV-Visible regions and Recording DR UV-Visible Spectrophotometer.

More particulars can be had from :

SOLE AGENTS :

TOSHNIWAL BROTHERS PRIVATE LTD.

198, Jamshedji Tata Road, BOMBAY-1

Branches :

14-B/4 N.E.A. Uttari Marg, NEW DELHI-5.

9, Blacker's Road, MADRAS-2.

31, Ballygunje Place, CALCUTTA-19

Printed by Sri Sibendranath Kanjilal, Superintendent, Calcutta University Press., 48, Hazra Road., Ballygunj, Calcutta and Published by G. Banerjee, Esq., M.Sc., Asst. Editor., Indian Chemical Society.